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THE ELECTRONIC THEORY OF VALENCY

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THE ELECTRONIC THEORY OF VALENCY

BY

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PREFACE

THIS book aims at giving a general account of the principles of valency and molecular constitution, founded on the Rutherford-Bohr atom.

In developing the theory of valency there are two courses open to the chemist. He may use symbols with no definite physical connotation to express the reactivity of the atoms in a molecule, and may leave it to the subsequent progress of science to discover what realities these symbols represent: or he may adopt the concepts of atomic physics—electrons, nuclei, and orbits—and try to explain the chemical facts in terms of these. But if he takes the latter course, as is done in this book, he must accept the physical conclusions in full, and must not assign to these entities properties which the physicists have found them not to possess: he must not use the terminology of physics unless he is prepared to recognize its laws. I have endeavoured to conform to this principle, and not to lay myself open to the reproach of an eminent physicist, that 'when chemists talk about electrons they use a different language from physicists'. I have been careful to avoid as far as possible the introduction of any physical hypotheses which are not already sanctioned by those who are best qualified to judge of them.

A theory of valency can only be justified by showing that it is applicable to chemistry as a whole; it is not enough that isolated examples can be quoted in its defence. In the present volume the general principles of the theory are discussed, and I propose in a second

volume to consider their application to the individual elements in detail; but as this cannot appear for some time, I have included here (Chapter XV) a summary of the characteristics of the several periodic groups, in the light of the results reached in the previous chapters. This must involve some repetition in the next volume, but it seemed desirable to indicate how these ideas can be used to elucidate the relations of the periodic table, and of inorganic chemistry generally.

It has been suggested that the development in the last few years of the theory of wave mechanics necessitates a fundamental change in our views of atomic structure. This theory, in the hands of de Broglie, Heisenberg, Schrödinger, and others, has had the most remarkable success in dealing with problems of atomic physics, and in particular has enabled us to calculate the relative intensities of spectral lines, which on the Bohr theory was possible only to a very limited extent. These results are obtained by treating the electron-in-its-orbit as a system of stationary waves, so that the electron as a separate entity seems to disappear from physics, and it might be thought that we are no longer entitled to speak, as we formerly did, of electrons as actual bodies rotating round nuclei. But the theory of wave mechanics, although there can be no doubt of its value as a calculus, has not yet reached the stage at which one can say definitely how it is to be translated into physics. It gives the right answer to problems hitherto treated as questions of probability and statistics, although it may be the statistics of a single atom. It has as yet given no proof that the physical concepts which led Schrödinger to his fundamental differential equation should be taken so literally as to be incompatible with the conceptions

of the nature of electrons and nuclei to which the work of the last thirty years has led.

Among the books which I have used I have especially to acknowledge my debt to Bohr's *Theory of Spectra and Atomic Constitution*, to Andrade's *Structure of the Atom* (of the third edition of which Prof. Andrade was so kind as to allow me to read the proofs before publication), to Stoner's *Magnetism and Atomic Structure*, and to G. N. Lewis's *Valence*: and on the chemical side to Abegg's invaluable *Handbuch*, Werner's *Neuere Anschauungen*, Weinland's *Komplexverbindungen*, and Pfeiffer's *Organische Molekülverbindungen*. Other monographs which I have consulted are referred to in their place.

I am also under great obligations to several of my friends for assisting me with their knowledge of the large range of subjects with which such a book as this necessarily deals. Prof. F. A. Lindemann has read and criticized the first three chapters, dealing with the physics of the atom, and greatly increased both their accuracy and their perspicuity; Dr. E. C. Stoner has helped me with the list of atomic structures and the chapter on magnetism; Mr. W. H. Mills has given me the benefit of his unrivalled knowledge and judgement in the chapters on stereochemistry and chelate rings, the latter of which has also profited by the criticisms of Mr. T. W. J. Taylor. Prof. T. S. Moore has read the whole book in proof, and made many useful suggestions. I owe an especial debt of gratitude to Mr. M. P. Applebey, who has not only read the whole of the manuscript with great care, and saved me from many errors and obscurities, but has also allowed me to read the manuscript of his lectures on inorganic chemistry, which have been of great value to me throughout, and particularly in the last chapter.

Mr. L. A. Woodward has helped me with the correction of the proofs and the preparation of the index. In gratefully acknowledging the assistance of so many kind friends, I feel bound to add that they are not to be held responsible for any of the views I have expressed, with which they by no means always agree.

I have further to thank Messrs. Bell and Prof. Andrade for permission to use the diagrams on pages 26 and 27.

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NOTE TO SECOND IMPRESSION

In this impression some misprints have been corrected, and a few ambiguities removed; but no substantial changes have been made.

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ABBREVIATIONS

Ann. Liebig's Annalen der Chemie.
Ann. Chim. Annales de Chimie.
Ann. d. Phys. Annalen der Physik.
Ber. Berichte der Deutschen Chemischen Gesellschaft.
Bull. Soc. Bulletin de la Société chimique de France.
C. R. Comptes rendus des Séances de l'Académie des Sciences.
Chem. and Ind. Chemistry and Industry.
J. Am. Ch. Soc. Journal of the American Chemical Society.
J. C. S. Journal of the Chemical Society.
J. de Phys. Journal de Physique.
J. pr. Chem. Journal für praktische Chemie.
Phys. Z. Physikalische Zeitschrift.
Proc. Nat. Acad. Sci. Proceedings of the National Academy of Sciences, Washington.
Z. anorg. Chem. Zeitschrift für anorganische Chemie.
Z. f. Phys. Zeitschrift für Physik.
Z. phys. Chem. Zeitschrift für physikalische Chemie.

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h = Planck's Constant ($6{\cdot}554 \times 10^{-27}$ erg-seconds).
E.A.N. = Effective Atomic Number (see p. 163).
Alk = Alkyl, C_nH_{2n+1}.
Ar = Aryl, aromatic radical, as C_6H_5.
Me = Methyl, CH_3.
Et = Ethyl, C_2H_5.

I

THE NUCLEAR ATOM AND ATOMIC NUMBER

IF we disregard mere speculation on the structure of matter, our knowledge of the atom begins with the promulgation of the atomic theory of matter by Dalton in 1808. This was followed in 1834 by Faraday's enunciation of the laws of electrolysis. For some time the full significance of these laws was not appreciated. It was first pointed out by Helmholtz,[1] who says: 'Now the most startling result of Faraday's laws is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity.'[2] Faraday's laws in fact correspond exactly to Dalton's laws of constant and of multiple proportions: they assert (1) that the amount (and sign) of electricity connected with an atomic or other ion is constant; and (2) that if an atom can form more than one kind of ion (as cuprous and cupric, or ferrous and ferric), then the amounts of electricity combined with the same atom have a simple ratio to one another—or, as we should now say, the amount of electricity combined with a gram-ion of any element is either 96,540 coulombs or some small integral multiple of that quantity.

It was not, however, until the last few years of the nineteenth century that any light was obtained on the question of the structure of the atom. During these years a series of advances of the greatest importance were made, which bore either directly or indirectly on the question. In 1894 came the discovery of the first of the inert gases by Rayleigh and Ramsay, followed in a short time by that of the others. In 1895 Röntgen discovered the X-rays, and this led two years later to the recognition of

[1] Faraday Lecture, *J. C. S.*, 1881, **39**, 277.

[2] 'The Faraday lecture, delivered by Helmholtz before the Fellows of the Chemical Society in the theatre of the Royal Institution on Tuesday, April 5, 1881, was an epoch-making monument of the progress of Natural Philosophy in the nineteenth century, in virtue of the declaration, then first made, that electricity consists of atoms. Before that time atomic theories of electricity had been noticed and rejected by Faraday and Maxwell, and probably by many other philosophers and workers; but certainly accepted by none. Now in the beginning of the twentieth century we all believe that electricity consists of atoms.'—Lord Kelvin, preface to the English translation of Königsberger's *Life of Helmholtz*, Oxford, 1906.

radioactivity by Becquerel. About the same time J. J. Thomson, Wiechert, and Kaufmann were engaged in investigating and interpreting the phenomena of the electric discharge in high vacua (Crookes's ' fourth state of matter '), and arrived in 1897 at the discovery of the atom of negative electricity—the electron. If our knowledge of atomic structure is still in many respects imperfect, as it is, it must always be remembered that thirty years ago we had no certain knowledge that the atom had any structure, and no evidence of the existence of anything smaller than a whole atom.

The evidence given by Thomson for his electronic theory was in outline this. Crookes had shown that when an electric discharge was passed through a highly exhausted tube, ' rays ' were sent out in straight lines from the cathode, which became evident when they struck the sides through the green fluorescence which they produced. Their rectilinear propagation was proved by interposing a screen, which cast a shadow in the same way as it would have done with rays of light. The nature of these rays was disputed, some maintaining that they were charged particles, and others that they were forms of vibration in the ether. The first view was maintained by Thomson, chiefly on the following grounds: (1) that they were deflected by a magnetic field in a direction perpendicular to the lines of force, as charged particles would be; (2) that Perrin had shown that if the stream of rays were deflected so as to fall on an insulated metallic surface, that surface acquired a negative charge; (3) that they were deflected by an electric field.

The methods by which their velocity, mass, and charge were determined are in principle very simple. A narrow beam of the rays is exposed to an electric field, and at the same time to a magnetic field. The two fields are so adjusted in strength that they exactly neutralize one another, and the spot of light produced by the rays is not shifted from its original position. Then we know that the forces exerted by the two fields are equal. Now if e is the charge on each particle, and v its velocity, the electric field of strength X will produce a force $X \cdot e$, and a magnetic field of strength H a force $H \cdot e \cdot v$. Thus at equilibrium

$$X \cdot e = H \cdot e \cdot v, \quad \text{or} \quad v = \frac{X}{H}.$$

As we can measure X and H, we can thus determine v, independent of the value of e.

The actual velocity of the electrons varies with the conditions

of their liberation, from zero (in the case of a hot wire) to 99·8 per cent. of the velocity of light, in the case of the fastest β-rays from radioactive substances ; by arranging the conditions, any desired velocity within these limits may be obtained.

The ratio of the electric charge to the mass can be measured most easily by abolishing the magnetic field and observing the deflection in an electric field alone. If X is again the strength of the electric field, the particle is being deflected exactly as a heavy body shot out horizontally is deflected by gravity, and its acceleration g is $\mathrm{X}\cdot\frac{e}{m}$. If it moves through a length l with the velocity v, the time during which it is exposed to the force is l/v, and hence d, the distance through which the spot of light moves when the field is put on, is

$$d = \frac{1}{2}gt^2 = \frac{1}{2}\frac{\mathrm{X}\cdot e}{m}\frac{l^2}{v^2}.$$

Hence $\frac{e}{m} = \frac{2dv^2}{\mathrm{X}l^2}$, where d, X, v, and l are all measurable. Thomson found that if the value of the charge e is assumed to be the same as that of the charge of a hydrogen or other univalent ion, the mass of the electron is 1/1840 of the mass of a hydrogen atom.[1] Subsequently, the actual number was counted, by the method of C. T. R. Wilson, of using them as centres of condensation of water vapour, and this view of their charge and mass confirmed.

On further investigation it was found that cathode rays could be produced by a great variety of methods—by electric discharge in high vacua, by the action of ultra-violet light on metals, in flames, from heated wires, by the action of X-rays, and from radioactive substances ; and it was shown by Townsend and others that by whatever methods and from whatever materials they were produced, though their velocity varied, their other properties, and especially the ratio e/m, did not. Thus it is clear

[1] This does not involve a knowledge of the Avogadro number N (the number of molecules in a gram-molecule) or of the weight in grams of a hydrogen atom. These experiments show that the charge on a gram of electrons is 18 million electromagnetic units. That on one gram of hydrogen ions is known to be 96,540 coulombs or 9,654 E.M.U. If each hydrogen ion has the same charge as one electron (of opposite sign) there must be in one gram of electrons $\frac{18{,}000{,}000}{9{,}654}$ or 1860 times as many electrons as there are hydrogen ions in one gram. (These values are only approximate : the exact mass of an electron is more nearly 1/1840 of that of a hydrogen atom.)

that the electron, with a negative charge of $4{\cdot}77 \times 10^{-10}$ E.S.U., and a mass of H/1848, is a constituent of every species of atom.

A variety of further discoveries of importance gave support to this view. In particular, the effect discovered by Zeeman, that when a body emitting light is placed in a magnetic field the spectrum lines are split up, was shown by H. A. Lorentz to be quantitatively explicable on the hypothesis that the emission of light is due to electrons of this charge and mass.

Now the atoms are electrically neutral, and so if they contain negative electricity in the form of electrons, they must also contain an equal amount of positive electricity in some form. The nature of this was for some time unknown. In his earliest attempts to deduce a structure for the atom, Thomson assumed that the electrons moved in a sphere of uniform positive electrification. This was avowedly pure speculation, but it enabled him to calculate that the successive electrons would arrange themselves in concentric rings, and even on certain assumptions in rings of eight, suggesting a recurrence of properties at periodic intervals in the series of elements, and a relation to the eight groups of Mendeléeff's table.

The discovery of X-rays, and of the rays accompanying radioactive change, provided new and powerful instruments for examining atomic structure. The difficulty of this problem is the difficulty of penetrating into the structure of the atom ; it is only by finding something that can get inside that we can discover what is there. Ordinary matter cannot penetrate into the atom, and the atom is so small in comparison with visible light that optical methods are of no use : the wave-length of yellow sodium light is about 3,000 times the diameter of an atom. But the X-rays are much shorter (wave length from about five to one-tenth atomic diameter), and hence they penetrate the atom and are affected by its various parts. The β-rays of radioactive substances are themselves electrons, and have enormous velocities, approaching in some cases that of light : while the α-rays are very small particles (as compared with the atom) as heavy as four hydrogen atoms, and have velocities which may rise to a tenth of that of light. These powerful agents can force their way inside the atom, and we can infer what is there from the effect which it has on them.

The first experiments carried out by these means were to direct a narrow parallel beam of one of these kinds of rays—β-rays from a radioactive source—on a thin sheet of metal. It is found that

the emergent beam is no longer parallel, but is divergent. This is the natural result of the repulsion of the β-particles by the electrons in the atoms of the metal. The amount of the divergence enables us to calculate how many electrons they have met in their passage, and therefore how many electrons there are per atom. It is found that this depends on the nature of the atom, and that the number is about half the atomic weight on the ordinary scale, say about 12 for aluminium, and about 100 for gold. It is thus clear that the freely moving electrons in an atom only account for a very small fraction (about 1 /4000) of its mass.

But in the course of this work a further discovery was made, which was of fundamental importance. Geiger and Marsden [1] exposed a gold leaf to a beam of α-rays. The average scattering was 0·87°, in agreement with the general result given above. But they found that a small number of particles suffered very large deflections, and some were even driven backwards. Thus 1 in 20,000 were deflected through large angles, the average value of which was 90°. Now from the mean value of 0·87° it can easily be calculated that the chance of a deflection of 90° is vanishingly small. Hence it is evident that a new phenomenon is taking place. This cannot be a surface reflection, because the number of particles so scattered increases in proportion to the thickness of the leaf. For the same reason it cannot be due to a succession of small deflections, because if it were, the number would increase only in proportion to the square root of the thickness, since we cannot assume that the successive deflections would all be in the same direction.

These facts were pointed out by Rutherford in a paper [2] which is the foundation of modern atomic theory and contains the statement of the doctrine of the nuclear atom. The α-particle weighs more than 7,000 times as much as an electron, and hence no collision with an electron (which cannot be moving very much faster than the α-particle) could do more than deflect it slightly. It can only be turned back by hitting something more or less of its own mass, and in order that sufficient force may be developed, this heavy particle must have a large electrical charge. Rutherford points out that ' the theory of J. J. Thomson ' (of the sphere of uniform positive electrification) ' does not admit of a very large deflection in traversing a single atom, unless it is supposed that the diameter of the sphere of positive electrification is minute in comparison with the diameter of the sphere of influence

[1] *Proc. Roy. Soc.* 1909, 82, 495. [2] *Phil. Mag.* 1911, 21, 669.

of the atom '. After considering the dynamics of the problem he shows that the determining factor is the charge Ne on this small positive nucleus, and that the value of this charge can be calculated from the amount of the wide-angle scattering. He finds for a series of elements values of N approximately equal to half the atomic weight, that is, equal to the number of free electrons in these atoms as deduced by Crowther from the scattering of β-rays, and subsequently by Barkla from that of X-rays. There can thus only be one of these nuclei in the atom, since its charge is equal to that of all the free electrons.[1]

Rutherford's theory therefore is that the atom consists of a small nucleus containing the whole positive electricity of the atom, and practically the whole of its mass ; this has a charge of $N \times e$ units of positive electricity, and is surrounded by N negative electrons, which form with it a neutral atom.

On this theory all subsequent developments of the theory of the atom have been built. The idea of a nuclear atom had been suggested earlier by several physicists, but without any evidence in its support. The evidence adduced by Rutherford is so simple and direct, that no serious effort has been made to dispute it.

It still remains to discover what the atom or unit of positive electricity is. Now the hydrogen atom contains the lightest nucleus known, and has one attendant electron. Its nucleus therefore has a charge equal to that of an electron. In a suitable discharge tube we can get positive rays consisting simply of the hydrogen atoms which have lost their attendant electrons. These are the lightest positively charged atoms which we can obtain. It is also noticeable that while most elements will give positive rays consisting partly of doubly and trebly charged atoms, the hydrogen atom can never acquire more than one positive charge. For these and other less direct reasons it is practically certain that the hydrogen nucleus is the actual unit of positive electricity corresponding to the electron, having the same charge but of opposite sign, and a mass of 1·007 (O = 16). This is known as the proton.

In his paper Rutherford drew attention to the great importance of the magnitude of the nuclear charge Ne as determining the properties of the atom. The importance of the number N became further emphasized as the result of two different lines of

[1] A further proof is that if there were several nuclei in the atom, the ratio of the specific heats of gases at constant pressure and constant volume could not be as high as 1·67 even for monatomic gases.

research. The study of radioactive changes showed that when an atom disintegrates, it gives off either an α-particle—a helium nucleus with a double positive charge—or a β-particle, an electron ; and the energy of these particles proves that they come from the nucleus. Early in 1913 it was pointed out simultaneously by Russell,[1] Fajans,[2] and Soddy,[3] that when an element undergoes an α-ray change it moves two places in the periodic table to the left (i.e. towards hydrogen) ; for example, radium in Group II becomes emanation in Group O : and when it undergoes a β-ray change, it moves one place to the right (towards uranium). This is what one would expect if every successive element had a nuclear charge one unit larger than that of its predecessor, the α-particle carrying off two positive charges and so reducing the charge on the nucleus by 2, whilst the β-particle removes one negative unit, and so increases the nuclear charge by 1.

The hypothesis that successive elements differed by one unit in their nuclear charge—that every possible nuclear charge from 1 to the highest known was represented by a different element—had been suggested quite definitely by van den Broek in 1911 ; [4] but as it was not supported by any very definite evidence, and indeed in its original form was related to an incorrect form of the periodic table, it did not attract much attention.

The radioactive evidence was confined in the first instance to the radioactive elements, and its applicability to the lighter elements was uncertain. The whole question took on a different aspect in the light of the work of Moseley in the same year.[5] He measured the wave-length of the X-rays given off by various elements when bombarded with cathode rays, by means of a potassium ferrocyanide crystal used as a grating. The full significance of his work can only be understood in relation to the Bohr theory of atomic structure ; but even without regard to this or any other theory, his results are sufficiently remarkable. He showed that the frequencies of the radiations were characteristic of each element : that if the square root of the frequency of the hardest ray (i.e. with highest frequency) was plotted against a value for each element called the atomic number, it

[1] A. S. Russell, *Chem. News*, 1913, **107**, 49 (Jan. 31).
[2] K. Fajans, *Phys. Zeitschr.* 1913, **14**, 131 (Feb. 15).
[3] F. Soddy, *Chem. News*, 1913, **107**, 97 (Feb. 28).
[4] *Nature*, 1911, **87**, 78 ; 1913, **92**, 372 ; *Phys. Zeitschr.* 1913, **14**, 32.
[5] *Phil. Mag.* 1913, **26**, 1024 ; 1914, **27**, 703.

gave a straight line : and that the atomic number required to give this relation is the ordinal number of the element in the series of elements arranged according to their atomic weights. This relation held for all the elements he examined—from aluminium (taken as 13, since it was the thirteenth of the known elements), to gold 79, except in three cases (A, K : Co, Ni : Te, I) where the order of atomic weights was already known to disagree with the order of chemical properties, and with the further proviso that four of these elements (43, 61, 72, 75) still remained to be discovered.[1] This conclusion is sufficient to show that, as he says : ' there is in the atom a fundamental quantity which increases by regular steps as we pass from one atom to the next. This quantity can only be the charge on the central positive nucleus.' If we apply the Bohr theory, we can show that the wave-lengths which he obtained agree quantitatively with those required by the theory, on the assumption that the known elements correspond to all possible integral values of the nuclear charge (with the exception of six, of which four have since been discovered) from 1 to 92.

We may summarize the conclusions so far arrived at as follows. All atoms are composed of positive units of electricity or protons and negative units or electrons : each of these has a charge of $\pm 4{\cdot}77 \times 10^{-10}$ electrostatic units. The mass of the proton is 1·007 (taking the weight of the oxygen atom as 16) and that of the electron is 1/1840 or 0·00054. The protons are all collected in a very small volume forming the nucleus, and are surrounded by a number of electrons sufficient to neutralize their charge. Thus the atomic number is at once the ordinal number of the element, the positive charge on the nucleus, and the number of electrons surrounding the nucleus. Now since practically the whole mass of the atom is due to the protons, and each of these weighs as much as a hydrogen atom, every atom must contain in the nucleus a number of protons equal to its atomic weight on the ordinary scale. The atomic number is about half this. Hence the number of protons in the nucleus must be about twice the nuclear charge. This means that the nucleus must contain electrons as well as protons—and about half as many electrons as protons—to neutralize part of its charge. For example, sodium, atomic weight 23, atomic number 11, must have 23 protons in the nucleus to give it its mass, and, therefore, 12

[1] There were (and still are) also two other elements missing beyond gold, 85 and 87 : in these the nucleus is probably too unstable to exist.

electrons also in the nucleus to neutralize 12 of them and leave a balance of 11 positive units. This nucleus (23+, 12−) is surrounded by 11 electrons, forming a neutral atom. In the same way iodine (atomic weight 127, atomic number 53) must have in the nucleus 127 protons and $127-53=74$ electrons; and this nucleus is surrounded in the neutral atom by 53 electrons. In general, an atom of atomic weight A and atomic number Z will have a nucleus of A protons and A − Z electrons, surrounded by Z other electrons.

At this point we may consider briefly the magnitude of the atom and its parts. It would take us too far to discuss the evidence for this; but it should be said that we make the assumption, which is now generally accepted, that the mass of the proton and of the electron is solely due to their electrical charge.

The number of atoms in a gram-atom—for example, of hydrogen atoms in 1 gram, or of sodium atoms in 23 grams (the Avogadro number)—is $6{\cdot}06\times10^{23}$. This figure does not convey much as it stands, but some idea of its meaning may be got from two facts. If a tumblerful of water is poured into the sea, and in the course of time this becomes uniformly distributed through the sea, the rivers, and all the other waters in and surrounding the earth: and if then a tumblerful of water is taken from any sea or river, this will contain about 1,000 of the molecules that were in the original tumbler. Another illustration has been given by Aston. Take an ordinary exhausted electric light bulb, and let a minute hole be made in the side, just big enough to let through a million molecules every second.[1] It will be 100 million years before the bulb is filled with air at atmospheric pressure.

To get an idea of the dimensions of the atom and its parts we must multiply them by some factor which will make them of a more familiar size. We may take the factor suggested by Darwin, 10^{13} : 10^{13} cms. is about two-thirds of the way to the sun. The dimensions are:

	Actual.	$\times 10^{13}$.
Diameter of atom .	$2-4\times10^{-8}$	2 − 4 kms.
electron .	$1{\cdot}88\times10^{-13}$	1·88 cms.
proton .	1×10^{-16}	1/100 mm.—barely visible.
nucleus (not hydrogen)	$3-30\times10^{-13}$	say 1 inch to 1 foot.

[1] The hole must be supposed to be gradually enlarged so as to keep this rate constant as the pressure inside the bulb increases.

So if we had one of these magnified atoms with its nucleus before us, the protons would be scarcely visible : the electrons would be about as big as sixpences or acorns (whatever their shape may be) and the nucleus, according to whether it was a light or a heavy atom, might be anything from the size of a cherry to that of a football. Round this nucleus the electrons would be revolving, the nearest pair (which produce the X-rays) a few feet off, and the farthest, which are the valency electrons, those that take part in chemical combination, moving in orbits which at their greatest distance are from half a mile to a mile away. The other planetary electrons would be distributed between these limits.

Perhaps the most surprising conclusion from these discoveries is the enormous proportion of the atom which is empty space. The density of the proton is about 10^{24} and that of the electron about 10^{11} times that of water. All the protons and electrons in the body of an average man if they could be brought close together would occupy less than a millionth of a cubic millimetre.

In considering the properties of the atom, and the parts played by different portions of its structure, we have to distinguish sharply between the nucleus and the electrons round it. The essence of the atom—its true individuality—resides in the nucleus. It is only under exceptional conditions that the nucleus can be altered, and when this does happen, a new element is formed. This is the real transmutation of matter. On the other hand, the surrounding or planetary electrons—or at any rate some of them—are quite easily removed and as easily replaced. Whenever an atom is ionized, whether by chemical combination, or by exposure under suitable conditions to the action of light, heat, or electricity, it gains or loses one or more electrons. For example, if a gas such as helium is ionized by heat or X-rays, the atoms split off one or more electrons leaving positively charged ions. When the exciting force is removed, the ion picks up a wandering electron, and returns to its previous neutral condition. But if the nucleus loses an electron, as happens in a β-ray radioactive change, the atomic number goes up by one : a new element has been formed, and the nucleus can never, so far as we know, regain the electron which it has lost. The loss of this electron (the β-ray) gives the atom a positive charge ; and this is soon neutralized by its taking up another electron : but the new electron does not go into the nucleus ; it takes its place among the planetary electrons, giving a neutral atom of atomic number one more than we started with.

The charge on the nucleus—the atomic number—determines the number of electrons which surround it, and also to a very high degree of approximation the shapes of their orbits : the mass of the nucleus has only a minute effect (see p. 23), since it is in any case large in comparison with that of the electrons, and the gravitational forces are negligible in comparison with the electrical. The chemical and (so far as they do not depend directly on the mass) the physical properties are determined by the number and shape of the electronic orbits, especially of those farthest from the nucleus, for when two atoms approach one another these external orbits are first affected, and their deformation shields the inner electrons, and still more the nucleus, from the influence of the other atom. Hence every atomic number corresponds to a definite set of chemical and physical properties, that is, in ordinary language, to a definite element. If an equal number of protons and electrons were added to the nucleus, its mass would be increased while its nuclear charge remained unaltered. This would lead to the production of what Soddy has called an isotope—an element of the same atomic number but a different atomic weight. Two isotopes will thus have the same number of planetary electrons, moving under the electrostatic attraction of the same nuclear charge. The difference in the mass of the nucleus must have some effect on the shape of the orbits and therefore on the chemical and physical properties of the atom ; but this effect is so small that it can only be detected with difficulty even in those properties which can be measured with the highest accuracy. The one element of which the isotopes can be obtained in any quantity in a state of approximate purity, so as to render this test possible, is lead. Lead is the final product of the radioactive change both of uranium and radium, and of thorium. The isotope formed from uranium should have an atomic weight of 206, and that from thorium of 208, as is shown by the following summary of the radioactive transformations (with the consequent changes of atomic number and weight) which these elements undergo :

At. No.	$92 - 16 + 6$		82
	$U - 8\alpha - 6\beta$	=	Pb : nucleus $206+, 124-$.
At. Wt.	$238 - 32$		206

At. No.	$90 - 12 + 4$		82
	$Th - 6\alpha - 4\beta$	=	Pb : nucleus $208+, 126-$.
At. Wt.	$232 - 24$		208

The atomic weight of ordinary lead is 207·2. Richards has obtained lead from cleveite of at. wt. 206·08, and Hönigschmid has got lead from thorite of at. wt. 207·9.[1] Richards has compared the properties of light uranio-lead with those of ordinary lead. He finds the melting points of the metals and the refractive indices of the salts to be identical. The density of the metal and the solubility of its salts as expressed in weight per cent. are exactly proportional to the atomic weights, from which it follows that the atomic volume and the molecular solubility of the salts are identical. The spectrum has been found by Aronberg [2] and by Merton [3] to show a definite but very small difference, approaching a hundredth of an Ångstrom unit. For all practical purposes therefore the isotopes may be regarded as identical in all properties not directly dependent on mass.

The theories of the nuclear atom and of atomic number are the foundation of modern atomic theory. The first established the dual nature of the atom ; it is composed of a minute central nucleus containing both protons and electrons, but an excess of the former : and this nucleus is surrounded by a cloud of electrons sufficient in number to restore the electrical neutrality. The concept of atomic number gives us as it were the empirical formula of the atom : it tells us what the charge on the nucleus is, and by how many electrons it is surrounded. There remains the question of the constitutional formula—of the arrangement of these electrical units ; and this again falls into two parts, the structure of the nucleus, and the structure of the surrounding electrons.

Of the structure of the nucleus comparatively little is yet known. Remarkable progress is being made in several directions, but the problem of investigating ' the inside of the inside of the atom ' as Rutherford puts it, is still in a very early stage. Moreover the problem is one which has only an indirect bearing on chemical questions, so that, in spite of its great intrinsic interest, it will not be further discussed here.

With regard to the arrangement of the electrons surrounding the nucleus, our knowledge is much greater ; and it is this part of the atom which determines the chemical behaviour. The only theory as to their distribution which can claim any physical basis

[1] Richards and Wadsworth, *J. Am. Ch. Soc.* 1916, **38**, 2613 ; Hönigschmid : see Fajans, *Z. Elektrochem.* 1918, **24**, 163 ; also Hönigschmid, ibid., 1919, **25**, 91.

[2] *Proc. Nat. Acad. Sci.* 1917, **3**, 710 ; *Astrophys. Journ.* 1918, **47**, 96.

[3] *Proc. Roy. Soc.* 1919, **96 A**, 388 ; 1921, **100 A**, 84.

is that of Bohr, which will be described in outline in the next chapter. This theory has had such a wonderful success in explaining the spectra—both optical and X-ray—of the elements, that its fundamental truth cannot be doubted, though we may, of course, expect that with further investigation it will undergo modifications in detail ; and its application to the chemistry of the elements is the main subject of this book.

II

THE BOHR THEORY: THE HYDROGEN ATOM

TWO years after Rutherford had brought forward his suggestion of the nuclear atom, Bohr produced his first paper on the subject.[1] He pointed out that such an atom was unstable on the ordinary principles of electrodynamics. In J. J. Thomson's model the electrons were assumed to be at rest under the combined influence of their mutual repulsions and the attraction to the centre caused by the uniformly distributed positive electrification, this latter force being proportional to the distance of the electrons from the centre. They would thus take up a stable group of positions, that is, one which would persist, and to which they would revert if they were disturbed from it. But in the Rutherford atom, in which all the positive electricity was collected at the centre, the electrons could not be at rest, or they would obviously fall into the nucleus. Rutherford supposed that they were rotating round the nucleus, whose attractive force was balanced by the centrifugal force acting on them, much as the planets are retained in their orbits against the sun's attraction; but he did not discuss the nature of the orbits in detail. Bohr pointed out that on the classical theory of electrodynamics such an arrangement could not be permanent. An electron moving in an orbit is a charged body subject to a continuous acceleration towards the centre of the orbit, and when a charged body is accelerated it must, on the Maxwell theory, radiate energy. Hence the electron should be constantly radiating energy and approaching the nucleus, and this process would only stop when it was actually in contact with the nucleus: that is, when the atom, having radiated an enormous amount of energy, had contracted to about a ten-thousandth of its original diameter.

Now some years before Bohr's paper was published, physicists had been compelled to recognize that the laws of ordinary dynamics could not be applied without modification to the processes of radiation. We must briefly consider the evidence which led to this conclusion, and the modification of these fundamental laws which it had been found to necessitate.[2]

[1] *Phil. Mag.* 1913, 26, 476.

[2] See Jeans, *Report on the Quantum Theory*, Physical Society, London, 1st ed. 1914, 2nd ed. 1924.

'Classical' dynamics—the dynamics on which we were all brought up—is founded on Newton's laws. It assumes that these principles, which can be verified (within the limits of experimental error) for the motions of the stars, and of masses of matter which we can handle, can be applied equally well down to the smallest quantities that exist. On this theory the motions and interactions of bodies are assumed to be continuous, and a body passing from one state to another is conceived to pass through an infinite series of intermediate states. Now it has been shown, primarily by Planck, Poincaré, and Jeans, that if these principles are applied to certain mechanical systems, they lead to results diametrically opposed to the facts. For example, suppose we have a volume of air enclosed by walls impermeable to energy, and containing a system of heavy particles, say shot, supported by springs. If the shot are set vibrating, and then the system is left to itself, we know that they will gradually communicate practically all their kinetic energy to the particles of air, whose velocity will thus be somewhat increased. This is generally expressed by saying that the friction of the air brings the shot to rest, and the air is thus slightly warmed. A dynamic investigation shows that according to Maxwell's theory of equipartition of energy the energy is ultimately so divided that each shot has as much as each air molecule : so that if there are twenty shot in a litre of air (3×10^{22} molecules), the shot will only retain 10^{-21} of their original energy. So far, theory and observation seem to agree. But in a vessel containing a gas there is besides the molecules of the gas something which we may call ether or we may call space, but anyhow something which is certainly capable of taking up energy in the form of radiation ; and this ether, if it is not continuous, must consist of particles far smaller than the atom. Here again by the equipartition principle the energy will distribute itself so that each ether particle has as much as a gas molecule ; and as the ether particles are far more numerous, nearly all the energy (all of it if the medium is continuous) ought to pass from the matter to the ether. But we know how energy is divided between matter and ether, and that in fact the matter has many million times as much as the ether (for example a mass of iron in a vacuum at 0° contains 8×10^{9} ergs. per c.c., and the ether only 4×10^{-21}). So there is clearly something wrong with our principles. But there is a further difficulty with respect to the ether itself. Just as most of the energy goes from the larger particles to the smaller,

so the energy of vibration in the ether will tend to pass from the longer to the shorter waves: and in radiation at equilibrium it can be shown that even on the most favourable assumption all except less than a millionth of the energy of the spectrum would be in waves shorter than the extreme ultra-violet. But the actual distribution is quite different: the maximum energy is at ordinary temperatures in the extreme infra-red, and even in sunlight (6000°) it is only in the yellow of the visible spectrum.

Many other examples might be given in which the deductions from classical dynamics are not in accordance with the observed facts. The light emitted by an incandescent gas is in some way connected with the motions of parts of the atoms, and since these, on the ordinary theory, can have an infinite number of orbits, the spectrum should be continuous: but in fact it is discontinuous. Again, the atomic heats of the elements should all have a value of about 6 from the absolute zero up to the ordinary temperature and above: but in fact they fall off rapidly at lower temperatures, approaching and sometimes reaching 0 (so far as can be observed) in the neighbourhood of the absolute zero.

It is thus clear that the old continuous dynamics, though it is quite satisfactory when we are dealing with large masses, breaks down when we apply it to atoms and their radiations. To meet this difficulty Planck in 1900 put forward his theory of quanta. He assumes that energy of vibration cannot be given out or taken up continuously, but only in definite portions, which he calls quanta of energy. These quanta are not atoms, in the sense in which we call matter and electricity atomic: their size is not fixed, but depends on the frequency of the emitting or absorbing body, or of the radiation, being equal to this frequency ν multiplied by a universal constant h, which has the value $6{\cdot}554 \times 10^{-27}$ erg-seconds. Thus for the D line of sodium (5890 Å.U., or $5{\cdot}89 \times 10^{-5}$ cms.):

$$\nu = \frac{3 \times 10^{10}}{5{\cdot}89 \times 10^{-5}} = 5{\cdot}09 \times 10^{14},$$

and the quantum, the product of this by h, is $3{\cdot}3 \times 10^{-12}$ ergs; this seems a small quantity, but it means that if 23 grams of sodium give out this quantum, they emit 50 kg. calories.

It must be observed that translational energy is not subject to quantum limitations: for a particle moving in a straight line

$\nu = 0$, and so $h\nu = 0$: the interchange in this case is so far as we know continuous.

This is the fundamental idea of the quantum theory, the truth of which is no longer in any serious doubt. Its justification, which cannot be further discussed here, lies in the enormous number of facts in molecular and atomic physics which it explains, and in the quantitative agreement in the values of the Planck constant h deduced from quite different classes of phenomena.[1] The mechanism of the quantum emission—the cause of this limitation of the transference of energy—is one of the outstanding unsolved problems of modern physics. But we are concerned now not with the cause, but with the fact itself.

The problem of atomic structure is precisely of the kind to which we should expect the quantum theory to apply. It was in connexion with the general question of radiation that the breakdown of continuous dynamics was detected, and it was to overcome this difficulty that the quantum theory was invented. We should expect a similar difficulty to arise in explaining the electromagnetic radiation of the electrons, and a similar solution through the application of the quantum theory to be applicable to this case also. This application was the subject of Bohr's paper of 1913.

As we have seen, he began by pointing out that the Rutherford nuclear atom is unstable on the classical theory of Maxwell: the electrons as they rotate in their orbits should on that theory be continuously radiating energy, and should, therefore, get nearer and nearer to the nucleus until finally they fall into it. As the dimensions of the atom prove that the electrons have not done this, the only alternatives are to suppose either that the electrons can under some conditions rotate without emitting energy, or they do not rotate at all.

If the electron is at rest, we have to call in some wholly un-

[1] 'The idea of quanta was first introduced by Planck nearly twenty-five years ago in order to account for the distribution of energy in the spectrum of complete radiation. Its triumphs in predicting or explaining successively the velocity of electrons emitted by metals under the influence of light, the atomic heats of solids at low temperatures, the chemical constants of the simpler substances, the spectral series of the lighter elements, the X-ray spectra of all the elements and the various atomic constants have assured it a permanent place in physical thought, and there can be little doubt that it forms the outstanding discovery of our generation.' (Lindemann, Aristotelian Society, 1924.)

known force to prevent it from falling into the nucleus, as in the static models of J. J. Thomson and Langmuir ; and as we have no means of knowing the laws of action of this force, we cannot hope to draw any useful deductions from it.[1] It therefore seems better to try what can be done on the lines of the quantum theory by assuming that the electrons do rotate, but that they do so without radiation of energy, and hence without contraction of the orbits. We are then dealing with a system subject to the action only of known forces : the Coulomb force between electrical charges, and the centrifugal force due to the inertia of the electrons.

Bohr's theory is based on two fundamental postulates.

1. He assumes that among the infinite number of orbits possible according to continuous dynamics, there is a series in each of which the electron can continue to revolve without radiation of energy : these he calls the stationary states, meaning not that the electron is stationary, but that the orbit is so. In any one of these states the electron is subject only to electrical and inertial forces, and so its orbit can be calculated in much the same way as that of a planet. These states are distinguished by the fact that in them the electron possesses an integral number —1, 2, 3, &c.—of quanta of energy, defined by the equation $E = nh\nu$, where ν is the frequency of rotation, h Planck's universal constant and n an integer.[2] This quantizing of the energy of the rotating electron, a very different system from the oscillator on which Planck had based his theory (of which the frequency was constant independent of the energy, and equal to that of the emitted radiation), was a bold assumption, guess, or inspiration, which was justified by the agreement of its results with the observed facts.

2. The second assumption is that the electron radiates energy (in the form of light or otherwise) only when it passes in a ' quantum jump ' from one of these stationary states to another

[1] The arguments in favour of the dynamic as opposed to the static model are summarized by Millikan in his Faraday Lecture, *J. C. S.* 1924, 125, 1411.

[2] This can be expressed by saying that the angular momentum is an integral multiple of $h/2\pi$: thus for a circular orbit

$$mvr = n\frac{h}{2\pi}$$

where m is the mass and v the velocity of the electron, r the radius of its orbit, and n an integer.

of smaller energy. If its energy in the first state is E_1, and in the second E_2, it must give out the difference $E_1 - E_2$, and the frequency of the emitted radiation [1] is assumed to be given by

$$h\nu = E_1 - E_2, \quad \text{or} \quad \nu = \frac{E_1 - E_2}{h}.$$

This second postulate involves a departure from the original quantum theory, in that Planck obtained his radiation formula for an oscillator the frequency of which was constant and independent of its energy, and equal to the frequency of the emitted light, while no such simple relation can hold for the atom. As the energy of the orbit increases, the frequency of rotation changes (with hydrogen it is inversely proportional to the cube of the quantum number); hence it is not the same in the orbit which the electron leaves as in that to which it goes, and neither of these values is in general identical with that of the emitted light. Einstein has, however, shown [2] that this extension of Planck's theory is legitimate, and satisfies the observed laws of radiation.

The application of these ideas to the hydrogen atom, in which there is only a single electron, is comparatively simple, and affords the strongest evidence of the truth of Bohr's theory. If we suppose an electron to approach the nucleus from infinity, it will begin rotating in a very large orbit ($n = \infty$), and will then jump successively to smaller orbits, emitting light each time as its energy diminishes, until finally it reaches the smallest orbit ($n = 1$). In any one orbit the attraction of the nucleus must balance the centrifugal force, and therefore we can calculate the orbit and find W, the work required to remove the electron from that orbit to infinity: this is $-E$, and increases as the electron approaches the nucleus: the difference between its values for any two orbits is the amount of energy ($E_1 - E_2 = h\nu$) which is evolved as radiation when the electron jumps from one of these orbits to the other.

The relative values of these constants for the successive (circular) orbits in a hydrogen atom can thus be calculated, and are very simple.

[1] It will be observed that on this theory, while the electron can lose several quanta in one 'jump', these appear only as a single quantum of emitted radiation.

[2] *Phys. Z.* 1917, 18, 121; quoted by Andrade, *Structure of the Atom*, 2nd ed. 1926, p. 353.

STATIONARY STATES IN THE HYDROGEN ATOM.

Quantum Number.	*Radius.*	*Frequency of Revoln.*	*Work E of Removal.*	*Velocity in Orbit.*
1	1	1	1	1
2	4	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$
3	9	$\frac{1}{27}$	$\frac{1}{9}$	$\frac{1}{3}$
4	16	$\frac{1}{64}$	$\frac{1}{16}$	$\frac{1}{4}$
n	n^2	n^{-3}	n^{-2}	n^{-1}

Bohr's second postulate was of enormous importance in that for the first time it gave a meaning to the complicated relations of line spectra. The accuracy of spectroscopic measurements (of the order of one in a million) had made it possible to discover very detailed relations among the various lines of a spectrum : but they did not in any way resemble those to be expected on the prevalent theory. It was supposed that the frequency of the emitted light was identical with that of some moving part of the atom, in which case one would expect to find some kind of harmonic relation between the frequencies of different lines. No such relation could be detected : but on the other hand it was found that the observed frequencies could be obtained by taking all possible differences between the members of a series of ' spectral terms ' characteristic of the element in question (Ritz's combination principle). No explanation of this remarkable result could be given until Bohr's second postulate made it clear that these terms were the energies of the stationary states divided by the Planck constant ($\nu = \mathrm{E}_1/h - \mathrm{E}_2/h$).

Thus for atomic hydrogen the work required to remove the electron from the nth orbit to infinity is proportional to $1/n^2$:

$$\mathrm{E}_n = \frac{\mathrm{R}h}{n^2}$$

where R is a constant which will be discussed later. Hence, when the electron jumps from the nth to the n_1th orbit the energy radiated

$$\mathrm{E}_n - \mathrm{E}_{n_1} = \frac{\mathrm{R}h}{n^2} - \frac{\mathrm{R}h}{{n_1}^2} = h\nu$$

or

$$\nu = \mathrm{R}\left(\frac{1}{n^2} - \frac{1}{{n_1}^2}\right).$$

Now in the spectrum of hydrogen there are a series of prominent lines known as Hα, Hβ, Hγ, &c., whose frequencies were

shown by Balmer in 1885 to be accurately expressed by the formula $\nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$, where $n = 3, 4, 5,$ &c. To give an idea of what is meant by accuracy in spectroscopic work, the observed and calculated values of some of these lines are quoted (the last line was not discovered until later).

BALMER SERIES.

		ν calculated.	*ν observed.*
Hα	$n = 3$	456 995 × 10^9	456 996 × 10^9
Hβ	$n = 4$	616 943	616 943
Hγ	$n = 5$	690 976	690 976
Hδ	$n = 6$	731 192	731 193
Hϵ	$n = 7$	755 440	755 441
. . .	. . .	. . .	. . .
'Hν'	$n = 20$	814 365	814 361

By the time of Bohr's paper two other series of hydrogen lines were known, the Lyman series in the ultra-violet and the Paschen series in the infra-red, to which a third, the Brackett series, has since been added: these are given with equal accuracy by the equations

$$\text{Lyman}: \quad \nu = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right): \; n = 2, 3, 4, \text{ &c.}$$

$$\text{Paschen}: \quad \nu = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right): \; n = 4, 5, 6, \text{ &c.}$$

$$\text{Brackett}: \quad \nu = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right): \; n = 5, 6;$$

all with the same value of R. The explanation evidently is that in the Lyman series the electron jumps to the first, in the Balmer series to the second, in the Paschen series to the third, and in the Brackett series to the fourth quantum orbit.

A further confirmation of the truth of the theory is that if we calculate the diameter of the first orbit to which the electron returns, and which in the ordinary unexcited state of the atom it occupies, we find it to be $1{\cdot}08 \times 10^{-8}$ cms., which is of the same order of magnitude as that deduced from quite different phenomena, such as the viscosity of the gas.

Again, Bohr showed that on his theory the constant R can be expressed in terms of other known constants thus:

$$R = \frac{2\pi^2 N^2 e^4 m}{ch^3}$$

where m, e are the mass and charge of the electron, Ne is the charge on the nucleus (N thus being 1 for hydrogen), and c is the velocity of light. The value of R from the spectroscopic data is $1{\cdot}09675 \times 10^5$. The value calculated for the right hand side of the equation from the most accurate data known when Bohr wrote is $1{\cdot}09 \times 10^5$ (the most recent values give $1{\cdot}096 \times 10^5$).

A further confirmation of great value arose as follows. In 1897 Pickering had observed in the spectrum of the star ζ Puppis a series of lines of the general formula $\nu = \mathrm{R}\left(\frac{1}{2^2} - \frac{1}{(n + \frac{1}{2})^2}\right)$, R having the same value as in the Balmer series. Rydberg naturally assumed from the close resemblance of this to the Balmer series that these lines also were due to hydrogen, and he predicted a series $\nu = \mathrm{R}\left(\frac{1}{(\frac{3}{2})^2} - \frac{1}{n^2}\right)$, one of which was actually discovered in a stellar spectrum. Fowler afterwards found a series $\nu = \mathrm{R}\left(\frac{1}{(\frac{3}{2})^2} - \frac{1}{(n + \frac{1}{2})^2}\right)$ in the spectrum given by a mixture of hydrogen and helium. No place could be found for any of these series in the hydrogen spectrum on Bohr's theory. Bohr, however, pointed out that there was no evidence that these lines were due to hydrogen : they occurred either in the spectra of stars, or in that of a mixture of hydrogen and helium. They might, therefore, equally well be due to helium, and in singly ionized helium He^+ we have a system of a nucleus and a single electron, resembling the hydrogen atom in every way except that the nucleus has a double charge (and the diameter of the orbit is only half that of the hydrogen orbit of the same n). Hence, in Bohr's formula for R, N is now 2, and the constant should be four times as large as for hydrogen. Thus the Pickering equation should be written

$$\nu = 4\mathrm{R}\left(\frac{1}{4 \times 2^2} - \frac{1}{4 \times (n + \frac{1}{2})^2}\right)$$

$$= 4\mathrm{R}\left(\frac{1}{4^2} - \frac{1}{(2n + 1)^2}\right).$$

(Lines corresponding to even values of the second term were not then known, since they lie so close to the Balmer lines : they have however since been observed.) So also in the other series, since all the denominators have to be quadrupled the half quanta disappear, and the lines are seen to be those required by the Bohr theory for singly ionized helium.

Shortly afterwards Fowler showed that the Pickering lines can be produced in a tube containing pure helium, and therefore must be helium lines.

No sooner had this difficulty been triumphantly overcome than another appeared. Fowler showed that the ratio of the constant for these ionized helium lines to that for hydrogen is not exactly 4 but is 4·0016. This is beyond the range of spectroscopic error. Bohr replied by pointing out that in the original deduction of R it had been assumed that the nucleus was at the centre of the electronic orbit, whereas of course the real centre is the centre of gravity of the system nucleus + electron : in other words the mass of the electron had been neglected in comparison with that of the nucleus. Since the latter is 1840 times as heavy as the former, the error is small : but for exact accuracy the Bohr value of R should be multiplied by $\frac{M}{M + m}$, where M is the mass of the nucleus, and m that of the electron. As this correction is larger for hydrogen ($M/m = 1840$) than for helium ($M/m = 7360$) the ratio of the constants will not be exactly 4 : 1 but will be 4·00163 : 1.

Yet a further verification of the theory for these two spectra was given by Sommerfeld. We have so far assumed the orbits to be circular, and on the simple Bohr theory the energy is the same whether they are circular or elliptical. Sommerfeld showed that if we take into account the change of the mass of the electron with its velocity (see next chapter, p. 25) the energy varies slightly with the excentricity. The difference is so small (for the Balmer lines the separation is only about one-fortieth of that of the D lines of sodium) that it cannot be detected in the ordinary spectroscope. But when the lines are examined with high dispersion it is seen that each really consists of several lines close together (' fine structure '), and Paschen, Wood, and others have shown that the separation of these components is exactly that required by Sommerfeld's theory.[1]

Thus with these two spectra, that of atomic hydrogen and that of ionized helium, the Bohr theory is able to calculate the position of the lines in every detail, and with exact accuracy. In none of the more complicated cases, not even with neutral helium or molecular hydrogen, can the theory yet be applied in the same detail ; but its success with the simpler spectra gives

[1] A still more recent refinement in the interpretation of the fine structure is referred to later, p. 34.

us confidence in its general truth; and even with the more complicated spectra it affords the only explanation yet suggested of their fundamental characteristics—the series relationships of the lines, the connexion between the arc and the spark spectra, and the whole character of the X-ray spectra from the original law of Moseley up to the most recent developments.

III

THE BOHR THEORY: ATOMIC STRUCTURE AND THE PERIODIC CLASSIFICATION

THE dynamical problem becomes much more complicated when we have to deal with atoms containing several electrons, and it is not possible here to do more than describe the results, with a general account of the methods by which they are reached.

The first question to be decided is what types of orbit are possible. On the simple Newtonian theory described above, the energy of the orbit is independent of the excentricity, and hence is the same for a circle as for an ellipse. Sommerfeld however pointed out that since in an elliptical orbit the nucleus occupies one focus, the electron comes nearer to the nucleus at one part of its orbit, and therefore will move quicker. This must (on relativity principles) cause its mass to increase, and so it can be shown that instead of continuing to move on the ellipse, the electron will go a little farther round the nucleus each time: so that the whole (approximate) ellipse, or its major axis, will slowly rotate (Fig. 1). The planet Mercury has a similar orbit, of which the perihelion moves forward 43 seconds of arc every century, or one complete revolution every 2·88 million years. This rotation of the ellipse is comparatively slow: with the hydrogen atom the electron traverses the ellipse some 40,000 times for every revolution of the major axis (with the planet Mercury the ratio is 12 millions to 1).

Thus the motion of the electron is really made up of two motions superimposed on one another, a simple elliptical motion, and a slower rotation of this ellipse round the nucleus. It follows that just as we must quantize the angular momentum of the electron in the ellipse, so we must quantize that of the rotation (precession) of the ellipse itself: we shall have a definite series of degrees of ellipticity, just as we have a series of values of the total energy. In other words, the orbit must be characterized by two quantum numbers, the principal n and the subsidiary k.[1]

[1] To avoid confusion from the different systems of notation employed, it should be observed that every orbit has an azimuthal quantum number n_a and a radial quantum number n_r: the total quantum number n is the

As a rough approximation it may be taken that the principal quantum number represents the major and the subsidiary the minor axis (more accurately the latus rectum). When the two are equal the orbit is a circle : when they are unequal it is an ellipse, and the more they differ the more excentric the ellipse is. With a nucleus of a given atomic number, all orbits of the same n have (as a first approximation) the same maximum diameter, and all of the same k the same minimum distance from the

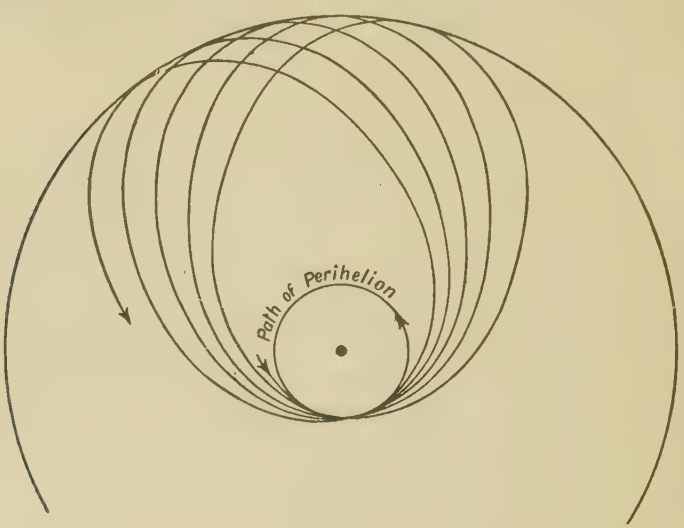


FIG. 1

nucleus. (All these statements need considerable modification in the case of atoms with large numbers of electrons.) The shape of the four possible orbits of principal quantum number 4 is shown (disregarding the precession) in Fig. 2.

The second quantum number can obviously have any integral value up to but not exceeding that of the first, and so if the latter is n there will be n possible kinds of orbit[1] n_1, n_2, n_3, . . . n_n. Bohr's object is to determine the values in terms of these two quantum numbers of all the orbits (the number of which is equal

sum of these two. In the 'n_k' system of Bohr n is the total and k the azimuthal quantum number. Thus :

$$\begin{aligned} n &= n_a + n_r \\ k &= n_a \\ n_r &= n - k \end{aligned}$$

[1] An n_o orbit is impossible, since it would be a straight line reaching the nucleus.

to the atomic number) of the electrons in the ' normal ' atom of any element. By the normal atom he means an isolated atom of the element at a temperature at which it has ceased to radiate, and all its electrons have returned to their lowest orbits.

Bohr's method is based largely on information afforded by the spectra of the elements, but also relies to some extent on the periodic table itself. We may begin by considering the lightest elements. In hydrogen we have the simplest possible atom :

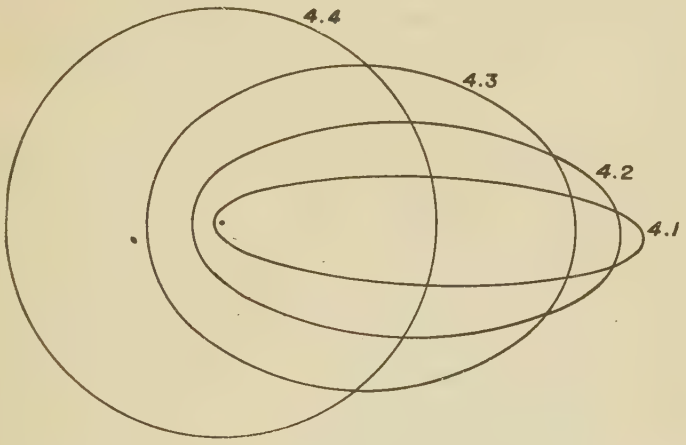


FIG. 2

there is only one electron, and this occupies a 1_1 orbit. In helium with a rise of the nuclear charge to 2, a second electron is taken up, which also occupies a 1_1 orbit, probably in a plane inclined to that of the first. (There is also another (metastable) arrangement possible with helium, but that cannot be discussed now.) These two electrons in 1_1 orbits (the K electrons) are also found in all the heavier elements ; this is proved by the validity of Moseley's law, that there is a constant relation between the frequency of the shortest X-ray line of an element and its atomic number. This line is due to an electron returning to the K (1-quantum) group : if at any point in the series of elements this group expanded and admitted more than two electrons, the relation would change at that point. The third electron introduced in lithium must therefore occupy an orbit of a different type. Already in helium the second electron is to some extent affected by the repulsion of the first, which partially neutralizes the attraction of the nucleus. If a third were introduced into

the 1-quantum group, the repulsion of the first two would be too great for it to remain there, even with the increased nuclear charge of 3. It therefore takes up an elliptical 2_1 orbit, in which for one part of its path it is actually inside the orbits of the K electrons, and exposed to the full attraction of the nucleus ; for the rest of its course it is outside the orbits of these electrons, which largely shield it from the nuclear attraction. While we can thus see a reason for the change in the type of orbit, we cannot yet calculate the forces exactly enough to say why it occurs precisely at this point ; but both the spectroscopic and the chemical evidence show that it does so. The same may be said of other conclusions of the Bohr theory, such as those given on p. 40.

In lithium, then, the third electron occupies a much larger (2_1) orbit than the first two, and the work of removal is far less, as is proved by the ionization potential (the potential difference required to give an electron sufficient velocity to remove an electron from the atom in the vapour) being only 5 volts, whereas for helium it is 25 volts. It is evidently the presence of this single easily removed electron which gives lithium its univalent character ; and the identical change in properties which we find when we go from any other inert gas to its succeeding alkali metal shows that a corresponding change of structure occurs in every case.

These conclusions indicate the important position which the inert gases occupy in the periodic scheme. They mark the points at which a quantum group has the number of electrons which it requires for stability. It is to this that they owe their chemical inertness ; their stability is so great that it cannot be increased by that redistribution of electrons between atoms which constitutes chemical combination.

Now the atomic numbers of the inert gases show a remarkable regularity :

	He	Ne	A	Kr	Xe	Em
Atomic number .	2	10	18	36	54	86
Difference . .	8	8	18	18	32	

They are all represented (Rydberg, 1914) by the expression $2(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2)$ taken to the necessary number of terms. This is a very striking fact. It reveals an unsuspected symmetry in the periodic table, far more remarkable than the rather forced arrangement in periods of 8 to which we are

accustomed. It is particularly to be noticed that the emanation,[1] which complies with the formula, lies beyond the confusing group of the rare earth metals, which are thus shown to form a perfectly regular part of the whole symmetrical table.

The results further indicate that the size of a stable group of electrons is always of the form $2n^2$, being 2, 8, 18, 32, and that the successive periods of the table, each ending in an inert gas, are due to the building up of these groups. At least it is evident that as we proceed along the first short period from helium to neon we are building up a group of eight 2-quantum orbits (2_1 ellipses and 2_2 circles), and that in neon this group is completed, and hence we have an element that is stable and chemically inert. The further development of the periodic table can be deduced either from the physical or from the chemical properties. The latter method was adopted by C. R. Bury,[2] who arrived independently at the same general conclusions as Bohr reached on physical grounds. The chemical argument may be given first, as establishing the main lines of development of the structure, although for the details we have to rely on the physical considerations advanced by Bohr.

If we disregard the smaller details of the periodic table, its general characteristics can be described, without reference to atomic structure, as follows. After hydrogen and helium we have the eight elements from Li 3 to F 9 and Ne 10 with a definite succession of properties. The second short period, containing the eight elements from Na 11 to Cl 17 and A 18, shows the same kind of development. After argon we have a period of eighteen elements up to krypton 36. This starts with potassium and calcium along the same lines as in the two preceding periods; but the following elements, although they have some resemblances to the corresponding members of the first two periods, go more and more off the lines, until we find the place of the eighth element, where we should expect an inert gas, occupied by the triad Fe, Co, Ni, to which there is no analogy among the earlier elements. This triad is followed by a series of eight, Cu, Zn, . . . Br, Kr, which, at any rate after the first member, show a close resemblance to the first group of eight. In the second

[1] The names radon, thoron, and actinon are now accepted for the three isotopic emanations. It is desirable that there should be some name for element no. 86 irrespective of any particular isotope, and I have retained the name emanation (with the symbol Em) for this purpose.

[2] *Journ. Amer. Chem. Soc.* 1921, 43, 1602.

long period (Rb . . . Ru, Rh, Pd : Ag . . . I, Xe) we have the same behaviour repeated.

In the next (very long) period of thirty-two we again start on normal lines with Cs, Ba : but we then find in La 57 to Lu 71 an entirely new kind of group, of fifteen successive elements—the rare earth metals—all trivalent and all very similar. The following elements Hf 72 to the triad Os, Ir, Pt 78 are just like the middle elements of the two long periods, and are followed by a group of eight (Au 79 to Em 86), which resemble the two short periods.

These relations suggest that the obvious idea that the order of the groups in the atom is the order of the successive increments from one inert gas to the next (and that emanation, for example, has the structure 2, 8, 8, 18, 18, 32) is wrong. If it were correct, we ought to get a wholly different type of development according to the size of the group which was being built up. In particular, we should not find as we do, that the type of growth in the first two short periods is repeated later in the seven elements preceding each inert gas. Now in the first short period we know that this is due to the building up of a group of eight electrons in orbits of the highest quantum number in the atom. We may conclude that the same thing happens at the close of the longer periods : that every inert gas has an outer quantum group of 8, and that krypton, for example, is not (2) (8) (8) (18), but (2) (8) (18) (8). If this is so, we must have in the first long period, which represents the passage to this structure of krypton from that of argon (2) (8) (8), not the formation of an external (4-quantum) group of 18, but the growth of the third quantum group from 8 to 18, followed by the formation of a new fourth quantum group of 8 (this is not exactly true, but we are now dealing only with the main outlines of the process). We can also see why there are ten elements instead of eight in the first section of the long period (from K 19 to Ni 28, at the end of the triad), since $18 - 8 = 10$. The same thing must occur again in the second long period : the 4-quantum group of 8 expands to 18 (Pd 46), and then a 5-quantum group of 8 is added, giving Xe as (2) (8) (18) (18) (8). In Em 86 we must again have the largest group in the middle, and an outer group of 8, giving (2) (8) (18) (32) (18) (8). The expansion of the fourth quantum group from 18 to 32 is a new phenomenon, involving fourteen elements : this is no doubt the cause of the unique series of rare earth metals from La 57 to Lu 71.

These conclusions, which were also arrived at on the physical evidence by Bohr, give us as the foundation of the table the following structures of the six inert gases :

Quantum Group .	1	2	3	4	5	6
He 2 . . .	2					
Ne 10 . . .	2	8				
A 18 . . .	2	8	8			
Kr 36 . . .	2	8	18	8		
Xe 54 . . .	2	8	18	18	8	
Em 86 . .	2	8	18	32	18	8

The fundamental principles of this system are two. (1) The maximum number of electrons that a group can contain is $2\ n^2$, where n is the principal quantum number. But the groups attain a state of comparative stability when they have eight or eighteen electrons, even if they are capable of holding eighteen or thirty-two. (2) In the stable structures of the inert gases the largest groups tend to be those of the middle quantum numbers, and the highest quantum group is always eight.

Before we discuss the structures in detail, we have to consider a recent development of the Bohr theory affecting a question which has not yet been raised, the distribution of the electrons of a group among the subgroups.[1] Bohr originally assumed that in a completed group the electrons were equally distributed among the subgroups : thus for the stable numbers 8, 18, 32 the arrangements were :

Orbits .	n_1	n_2	n_2	n_3		
	4	4	—	—	=	8
	6	6	6	—	=	18
	8	8	8	8	=	32

The maximum number of electrons in a group being $2\ n^2$, and of subgroups n, it followed that the maximum number of electrons in a subgroup was $2n$. This conclusion was based on general

[1] A group means all the electrons in an atom whose orbits have the same principal quantum number ; the term ring, which is often used instead, is less suitable because it suggests that the orbits of different groups are quite separate from one another, whereas in fact they are largely inter-penetrating. A subgroup consists of the orbits of the same principal and subsidiary quantum numbers. For the electrons whose orbits also have the third quantum number (discussed below) the same, we may use Andrade's term ' grouplet '.

principles of symmetry. Later work has shown that it needs modification. While the subgroups retain the meaning and importance which Bohr assigned to them, a different distribution of the electrons between them must be adopted. This is primarily due to the discovery that for a complete specification of the orbits two quantum numbers are not sufficient, but a third must be introduced. The most direct evidence of this is derived from a study of the X-ray absorption spectra. These differ from the 'optical' absorption spectra in one important respect, which needs a few words of explanation.

When a beam of radiation falls on an atom it will, if its frequency, and therefore its quantum, is large enough, disturb one or more electrons from their orbits, and drive them into outer orbits, or even away from the atom altogether (ionization); the process is in general the reverse of that of light-emission, which we considered in the last chapter. This expenditure of energy causes the removal from the beam of the radiation of a particular wave-length, and an absorption spectrum is produced. X-rays differ from 'optical' radiation—a term used to cover the infra-red, visible and ultra-violet—only in degree, being of much shorter wave-length, mostly from 10 to 0·1 Å.U., while the optical spectrum ordinarily measured is from 100,000 to 1,000 Å.U., intermediate wave-lengths (1,000–10) being much more difficult to measure (1 Å.U. = 10^{-8} cm.). The X-ray quanta are proportionally larger, and are able to remove the firmly bound innermost electrons of an atom, while the optical spectra correspond to the energies required for changes in the most loosely attached electron of the outer group. Thus the ordinary optical absorption spectra of gases are due to the shifting of these outer electrons to still more distant orbits, and as every such shift involves a definite expenditure of energy, the spectrum consists of a series of dark lines. (In a liquid or solid these lines are broadened out into bands, through the disturbing influence of the electric fields of neighbouring atoms.) The X-ray absorption spectrum is of a different form. If the radiation is hard enough (i.e. of short enough wave-length) to displace an electron from one of the inner groups in a heavy atom, this cannot go to a neighbouring group, because all these are full: it must either go to the outermost group or leave the atom entirely; and the difference between these two shifts is scarcely measurable. Hence, when atoms are struck by 'white' X-ray radiation (radiation having a continuous spectrum) absorption only begins

when we reach a frequency great enough to expel the electron. But the rather harder radiation beyond this is also able to expel the electron, and the excess of its quantum over the energy required for the expulsion is taken up by the electron in the form of kinetic energy. If the wave-length is shorter still, the electron is again expelled, with a greater velocity. Thus instead of a sharp line we get in the absorption spectrum a band with a sharp edge at the point where the energy becomes just sufficient for the removal of the electron in question. This is what is meant by the ' absorption edge ' of such a spectrum. By measuring these edges for the inner group of a heavy atom we can determine the work needed to remove electrons from every kind of orbit in the completed groups : the values so obtained are called the energy levels of the atom : they correspond to the ' spectral terms ' of the optical spectra.

On the original Bohr theory the number of energy levels for every group must be identical with the number of subgroups, and hence equal to the principal quantum number. But on examination it is found that the actual number is larger than this. In the first (K) group there is only one level, as the theory requires, but in the second (L) there are three instead of two (2_1, 2_2), in the third (M) five instead of three, and in the fourth (N) seven instead of four : in fact the number of kinds of orbits in the nth quantum group is not n, as the theory requires, but $2n - 1$.[1]

Thus it is clear that the Bohr (n_k) system, with its two quantum numbers, is insufficient to account for the variety of orbits which actually occur, and that a third quantum number j must be introduced and an n_{kj} system adopted. The physical meaning

[1] As an illustration, the following list of the energy levels of uranium is quoted from Siegbahn. They are expressed in terms of ν/R, and so are proportional to the energy of removal (the P levels are too close together to be differentiated).

Group	1 (K)	2 (L)	3 (M)	4 (N)	5 (O)	6 (P)
No. of electrons in group	2	8	18	32	18	12
Energy levels, ν/R	8477·0	1603·5	408·3	106·6	23·9	1·7
		1543·0	381·3	95·2	18·1	
		1264·2	317·2	76·4	11·8	
			273·9	56·2	7·5	
			261·0	53·8	5·8	
				28·2		
				27·4		

of this third number is not yet clear: but it must be remembered that the accuracy of spectroscopic data is so great that it is legitimate to introduce a term of this kind if it enables us to calculate the results quantitatively, even if we cannot give it a physical interpretation. Whatever j is, it is something which can never have more than two values for any given values of n and k. It was originally suggested that it represented the orientation of the orbit with respect to the axis of angular momentum of the atom as a whole. Recently, however, Sommerfeld and Unsöld [1] have shown that the introduction of a third quantum number makes it possible to explain in every detail the fine structure of the spectra of atomic hydrogen and ionized helium, including the occurrence of lines apparently forbidden by the correspondence principle,[2] the relative intensities of the lines, and their behaviour in a magnetic field (Paschen-Back effect). Since therefore j holds for a system of a nucleus and a single electron, it cannot depend on the orientation of electronic orbits. A more probable suggestion, favourably regarded by Bohr, is that it represents the direction of spin of the electron round its own axis.[3]

Whatever the meaning of j, it must, in order to account for the observed atomic levels, have two values for every n_k subgroup except those in which $k = 1$. A scheme of distribution of the electrons among these levels was suggested in 1924 independently by Main Smith [4] and by Stoner,[5] the former basing it chiefly on chemical arguments (which however are very difficult to follow), and the latter on physical evidence derived from the spectra and the magnetic properties. The necessary number of levels is obtained by following the rule that j is either equal to k or is one less. We thus get in any Nth quantum group a series of levels N_{11} : N_{21}, N_{22} : N_{32}, N_{33} : N_{43}, N_{44} : &c., in which the colons mark off the Bohr n_k subgroups. If we make one further assumption, that the maximum number of electrons in any level is twice the third quantum number, the size of the various quantum groups is accounted for, since we have :

[1] *Z. f. Physik*, 1926, **36**, 259.

[2] This principle of Bohr's is a limitation of the number of transitions possible among the orbits of an electron. In particular it requires that in every transition k should change by ± 1. It was originally derived from a 'correspondence' between the results of classical and quantum dynamics.

[3] Uhlenbeck and Goudsmit, *Nature*, 1926, **117**, 264; Bohr, ibid. See also Eddington, Richardson, Lindemann, and Frenkel, ibid. 652–4.

[4] *Chemistry and Industry*, 1924, **43**, 323.

[5] *Phil. Mag.* 1924, **48**, 719.

Level	N_{11}	N_{21}	N_{22}	N_{32}	N_{33}	N_{43}	N_{44}	
Maximum number	2	2	4	4	6	6	8	
N = 1	2	—	—	—	—	—	—	= 2
N = 2	2	2	4	—	—	—	—	= 8
N = 3	2	2	4	4	6	—	—	= 18
N = 4	2	2	4	4	6	6	8	= 32
n_k subgroups	2	6		10		14		

This classification is in entire agreement with the optical and X-ray data, those transitions alone occurring in which k changes by ± 1, and j either changes by ± 1, or remains unaltered.

It will be seen that this scheme, which is now generally accepted, retains the Bohr n_k classification, but carries out a further subdivision. It appears that the importance of this subdivision is less than that of the Bohr subgroups : levels differing only in the third quantum number are less easy to distinguish, and it is not yet possible to say how many of the orbits of an incomplete n_k subgroup belong to each of the two n_{kj} levels (' grouplets '). Hence the essential correctness of the Bohr classification is maintained, but with two important modifications. Firstly, the number of electrons in each subgroup is different : in place of (4, 4), (6, 6, 6), (8, 8, 8, 8), we have (2, 6), (2, 6, 10), (2, 6, 10, 14). Secondly, the development of the groups in the periodic table acquires rather a different significance : whereas Bohr supposed, for example, that the two subgroups of 4 in the fourth quantum group in krypton expanded to (6, 6, 6) in xenon, and to (8, 8, 8, 8) in emanation, we now have to realize that the grouplets present in the lighter atoms still persist in the heavier, and that the grouplets $2\times 4_{11} + 2\times 4_{21} + 4\times 4_{22}$ which occur in krypton are still present in xenon and emanation, though with the addition first of $4\times 4_{32} + 6\times 4_{33}$, and then of $6\times 4_{43} + 8\times 4_{44}$. This applies particularly to the pair of electrons of N_{11} orbits, which was not recognized by Bohr except in the first quantum group : this pair, which in helium (N = 1) constitutes an absolutely complete group, recurs on the new scheme at the beginning of all the other groups, and we shall see that it can under suitable conditions acquire, even in the groups of higher quantum number, something of the stability which it possesses in helium.

Before we consider the application of these principles to individual elements, something must be said of the peculiarities of the optical spectra, from which so much of the evidence for the

atomic structures is derived. The lines of the optical spectrum are due to the return of the most loosely bound electron in the atom from a higher (excited) orbit to a lower, and their frequency is proportional to the difference of energy of the two orbits. The same atom can give different spectra according to the means adopted for exciting it, and these are known as arc and spark spectra. In the arc the excitation is due to the high temperature, and the consequent collisions of the rapidly moving atoms with one another : these drive the outer electrons into higher quantum orbits, but as a rule do not detach them from the atom. Hence the radiation is due to neutral atoms. In the spark the energy is communicated to the atom mainly by swiftly moving electrons ; these are capable not only of exciting the neutral atoms, but also of removing one or more electrons from them completely—of ionizing them—and then of further exciting the ions so produced. The spark spectrum thus contains other lines (spark lines or enhanced lines) produced by these ionized atoms. The spectrum of a neutral atom X is known as X I, that of the atom X^+ which has lost one electron as X II, that of X^{++} as X III, and so on.

Now an excited atom, in which one electron has been driven into a higher quantum orbit, a large part of which is far removed from the nucleus and the other electrons, has a certain resemblance to a hydrogen atom. The excited ' optical ' electron is under the influence of the nucleus with its charge of $+N$ units surrounded by $N-1$ electrons (where N is the atomic number) ; when it is in the outer parts of its orbit, these are relatively at about the same distance from it, so that their effect is approximately equivalent to that of a single positive unit. It is for this reason that the arc spectra of other elements can be represented by formulae resembling (especially for the terms of higher quantum number) the Balmer formula for hydrogen, and with the same constant R. If, however, the excited electron belongs to an atom which has already lost an electron and is a singly charged positive ion X^+, the equivalent positive charge on the rest of the atom is not $+1$ but $+2$ $(N-(N-2))$, and in the formula, as in that of the He^+ spectrum, we must substitute $4R$ for R. If the atom has lost two electrons (X^{++} or X III), the electron is moving round a residue with a net charge of $+3$ units, and the constant is $9R$. Generally, the X S spectrum, which is due to atoms of X which have lost $S-1$ electrons, requires a constant S^2R.

These considerations apply as a first approximation only, and the spectra of individual elements all have their own peculiarities, which are often very complicated. In particular, the lines tend to occur in close ' multiplets '—sets of 2, 3, or more—the number being constant in a given spectrum, or at least in a given spectral series. The degree of multiplicity, the cause of which cannot be discussed here, is closely related to the position of the elements in the periodic table, the arc spectra of the alkalis giving doublets, and those of the alkaline earths triplets, and generally the odd periodic groups giving even multiplicities, and vice versa. When a spark spectrum is examined it is found that it closely resembles the arc spectrum of the preceding element, if allowance is made for the change in the constant : thus the spark spectrum of magnesium (Mg^+) is like the arc spectrum of sodium, but with the frequencies about four times as great, and while the arc spectrum of magnesium contains triplets, its spark spectrum, like the arc spectrum of sodium, contains doublets. The process has been carried farther : under more intense excitation it is possible to remove more electrons, and obtain the spectra of doubly and trebly ionized atoms [1] (Fowler, Paschen) ; and the rule still holds that the spectrum resembles that of the neutral atom with the same number of electrons, allowance being made for the increased constant S^2R. Thus we get the following series, in which the vertical groups represent similar spectra :

Electrons.	11	12	13	14
	Doublets.	*Singlets and triplets.*	*Doublets.*	*Singlets and triplets.*
Constant.				
R	Na	Mg	Al	Si
4R	Mg^+	Al^+	Si^+	
9R	Al^{++}	Si^{++}		
16R	Si^{+++}			

This rule, which is known as the spectroscopic displacement law of Kossel and Sommerfeld, illustrates the principle of atomic number (an increase of one as we pass from one element to the next in the table) for the planetary electrons in the same way

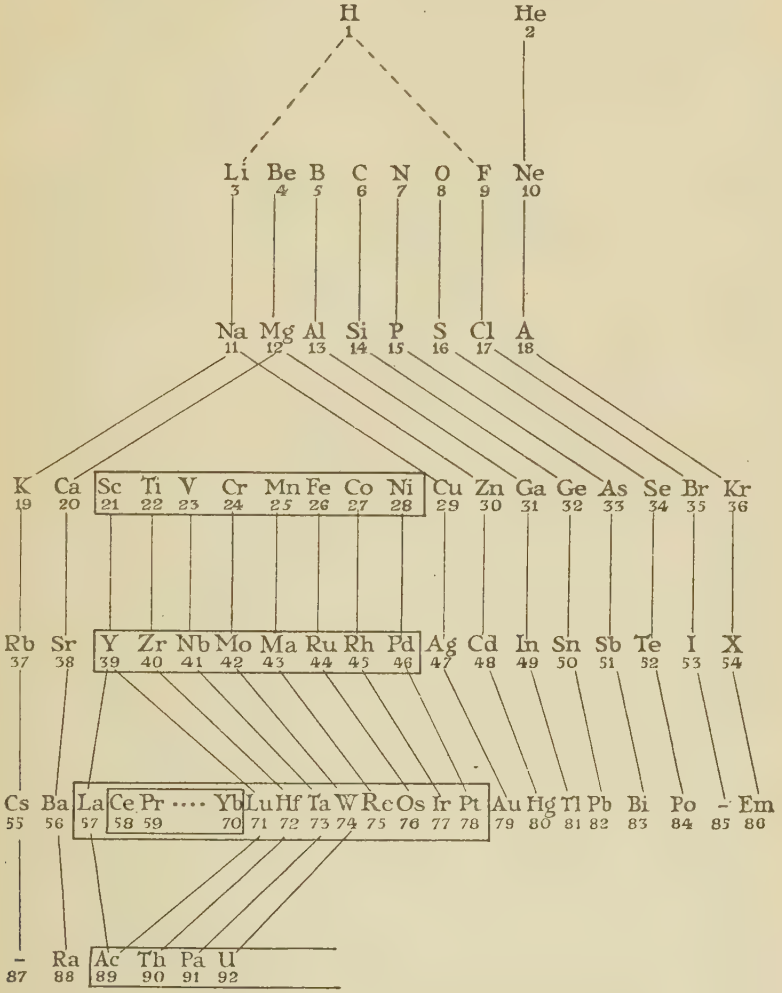
[1] The spectra of even more highly ionized atoms (up to Cl VII—i.e. with 6 electrons removed) have been obtained by Millikan and Bowen by the ' hot spark ' method, in which the pressure is reduced below 10^{-3} mm., so that a high voltage produces only very short sparks (2—0·1 mm.) of very great intensity.

as the radioactive displacement law of Russell, Fajans, and Soddy (p. 7) does for the nuclear charge. It is important from other points of view as well. It emphasizes the remarkable stability of the atomic structures, which are seen to retain their form even with considerable variation of the strength of the positive field in which the electrons move. This stability is one of the most marked characteristics of the atom, and the physical theory cannot as yet fully account for it. Of equal importance is the fact that in certain parts of the periodic table the displacement law no longer holds: certain electronic structures are possible only with particular values of the nuclear charge. This occurs at those points at which a development of a quantum group from one stable form to another (from 8 to 18, or from 18 to 32) is beginning, where it can be shown that the arrangement of a given number of electrons is changed when the nuclear charge is increased. The direction of the change is always the same: the increase of the atomic number brings the electron into an orbit of lower principal quantum number and greater excentricity (e.g. from 4_1 to 3_3). The cause of this change will be further discussed under scandium (below, p. 40). The spectrum evidence in this way affords a valuable proof of the exact point in the series of elements at which the development of the quantum group begins.

We may now consider the application of these principles to the periodic table[1] in more detail. The simplest method is to take the elements in the order of the atomic numbers. Hydrogen ($1 \times 1_{11}$) and helium ($2 \times 1_{11}$) have already been discussed. In the next two elements (Li 3, Be 4) the spectra show that first one and then two electrons in 2_{11} orbits are added, so that in beryllium the 2_{11} subgroup is full, and it remains unchanged in all subsequent elements. That the last electron in boron (5) cannot occupy the same subgroup as the previous two was concluded by Bohr on the analogy of aluminium, for which the spectrum shows that one of the three electrons in the highest quantum group is in a different kind of orbit from the other two: this has since been proved spectroscopically for boron, and is now, of course, a necessary

[1] The general relations are shown in the periodic table given on p. 39, which is taken from Bohr. The frames enclose elements in which the inner group is in a state of incomplete development: the lines connect elements which have their imperfect groups of the same size. The rare earth metals between Pr 59 and Yb 70 are omitted for convenience. The electronic structures of individual elements, according to the most recent results, are given on p. 48.

consequence of the classification of Stoner and Main Smith: the fifth electron must occupy a 2_2 orbit of one or other kind. The succeeding elements C, N, O, F have respectively 2, 3, 4,



and 5 electrons in the 2_{21} and 2_{22} levels, though we cannot be sure how they are distributed between them. In neon (10) these levels are full, with 2 in 2_{21} and 4 in 2_{22}. The second quantum group has now received the largest number of electrons that it can hold, and no subsequent change occurs in it.

In the second short period (Na 11 to A 18), the same process of

development is exactly repeated in the third quantum group. We thus reach argon, which is (2) (224) (224).

In the next period we begin as before by adding first one and then two electrons (in K 19 and Ca 20) to the new (fourth) group, so that up to this point (with a nuclear charge of 20) the third quantum group remains imperfectly developed, with the 3_3 subgroup unoccupied. But this must soon begin to fill, and Bohr has pointed out the exact place at which this happens. In the arc spectrum of potassium we have a measure of the energy differences of the various possible orbits of the nineteenth (last added) electron, moving round a nucleus of charge 19. From this we can deduce that it is about twice as firmly bound in a 4_1 as in a 3_3 orbit. In the spark spectrum of calcium (singly ionized) we are again dealing with the nineteenth electron, but now the nuclear charge is 20. Here we find that the electron is only very slightly more firmly bound in a 4_1 than in a 3_3 orbit.[1] It is evident that if we could measure the spectrum of doubly ionized scandium (19 electrons, nuclear charge 21), we should find that the 3_3 orbit was more stable than the 4_1. Hence the expansion of the third quantum group must begin with scandium, which will have two 4_1 electrons and one 3_3—all three however much more loosely held than the remaining eighteen. The reason for this change of orbit of the nineteenth electron can be given in general terms. The previous eighteen are arranged in an argon structure. When the nuclear charge is 19 (K), the positive field outside these eighteen is comparatively weak, as their screening effect neutralizes nearly the whole of the attraction of the nucleus : hence the electron is drawn into a long elliptical orbit, for part of which it comes into the powerful field close to the nucleus. A rise in the nuclear charge to 20 (Ca) increases the strength of the field near the nucleus by 5 per cent., but nearly doubles that of the external field. Thus there is much less difference between the field inside the argon group of eighteen electrons and that outside in calcium than in potassium, and still less in scandium. A point will, therefore, be reached at which a circular 3_3 orbit lying wholly outside the orbits of the first eighteen electrons becomes more stable than a 4_1, which penetrates far inside them : and the spectra show that this point is reached in scandium, where the nuclear charge is 21. On the other hand the screening effect of this nineteenth electron

[1] See Bohr, *Theory of Spectra*, p. 102, where diagrams of the spectra are given.

weakens the field outside its own circular orbit, so that the subsequent (twentieth and twenty-first) electrons in scandium will again occupy long 4_1 orbits.

In the following elements up to zinc (30) there is no reason to think that any increase in the fourth quantum group beyond two takes place ; indeed it is probable that in some (Cr and Cu) it is reduced to one. The elements from scandium (21) to nickel (28), which according to Bohr have not only the outermost but also the next quantum group incomplete (and which are distinguished in the table, p. 39, by being enclosed in a frame), have remarkable properties both physical and chemical. With the exception of scandium, of which the (trivalent) ion should properly stand outside the frame, they all have variable valency, their ions are coloured and are paramagnetic, and they all have a marked catalytic power. The variable valency obviously depends on the fact that the work required to detach one or more of the 3_3 electrons is not so much greater than that needed for the 4_1 electrons but that it can be effected by chemical agencies : so that the number of electrons which can serve for valency purposes can be varied. The colour also results from the incompleteness of the group. A coloured ion is one which absorbs light of the visible spectrum, and hence it must be capable of an electronic transition of which the energy corresponds to a quantum of visible light—something between 40,000 and 70,000 calories per gram-atom. In an ion like Na^+ or Ca^{++}, where the outer group is complete, the only possible transition is to a higher group, but to transfer an electron from a completed group to another would consume far more energy, and cause absorption in the ultra-violet. This is illustrated by the behaviour of sodium. The metallic vapour, in which the atom retains its valency (3_1) electron, is coloured : it absorbs in the yellow (the D line), owing to the transition $3_1 \rightarrow 3_2$. But the sodium ion, from which the valency electron has been removed, and in which only the very stable complete groups (2) (8) remain, is colourless. The simple ions of the metals from titanium to nickel all contain an incomplete third quantum group, and hence allow of transition from one level of this group to another, in which the absorption of energy is small, and causes absorption in the visible spectrum. The paramagnetism of these ions is due to similar causes, though we do not know so much about them. The ions with completed groups are diamagnetic because the magnetic moments of the various orbits balance one another ; but where

the group is imperfect this balance is not attained. The catalytic properties, which are equally well marked, are presumably connected with the variation of valency.

These properties also enable us to determine where the development of the third quantum group is complete. Copper (29) has one more electron than is required to complete this group. The cuprous ion might therefore be either (2) (8) (17) 1 or (2) (8) (18). That it has the latter structure, with the third group complete, is proved by its being colourless and diamagnetic. On the other hand the eighteen group in this atom, with a nuclear charge of 29, is not so firmly held that it cannot be broken into by chemical forces, and the cuprous ion can be converted into the cupric Cu^{++} = (2) (8) (17). Here we have the incomplete group again, and the colour and the paramagnetism reappear. In the next element zinc (30) the increased nuclear charge holds the eighteen group too firmly for it to be broken into, and accordingly zinc is always divalent, colourless, and diamagnetic.

Thus the general development of the series Sc 21–Zn 30 is clear, and the beginning and end of the transition are sharply defined. The question whether there are always two electrons in the fourth group has been disputed : the answer depends on the spectrum evidence. The most recent work [1] confirms Bohr's view that there are two, except in chromium, where there is probably only one. In copper the arc spectrum shows mainly the lines of an atom (2) (8) (18) 1, as we should expect from the existence and properties of the cuprous ion, but there are also lines which indicate the presence of atoms (2) (8) (17) 2 in equilibrium with the others.

The remaining elements from Zn (30) to krypton (36) have the same relations as those of the first two short periods.

In the second long period (Rb–Ag–I, Xe) the development resembles that of the preceding period, though not quite so closely as was at first supposed. In Rb 37 and Sr 38 we have as we should expect one and two electrons in the new (fifth) group, and in Y 39 the fourth group begins to expand. But there is evidence from the spectra [2] that the imperfect eighteen group is more stable when the principal quantum number is 4 than when it is 3 : and in particular that while Fe is (2) (8) (14) 2, Ru is (2) (8) (18) (15) 1, and while in nickel it is clear that two electrons are lacking to the eighteen group, the arc spectrum of palladium makes it

[1] Grimm and Sommerfeld, *Z. f. Physik*, 1926, **36**, 36 ; Sommer, ibid. **37**, 1.

[2] See Sommer, *loc. cit.*

probable that in the 'normal' atom this group is complete: Pd 46 = (2) (8) (18) (18). At what stage one of the two fifth quantum electrons which must be present in strontium is recalled to the fourth group is uncertain: according to Sommer this must happen at least by the time we reach zirconium. The greater stability of the eighteen in the fourth quantum group is shown by the behaviour of silver: this, as we know, differs from its analogue copper in that the eighteen group cannot be broken into by chemical means at all: it invariably gives a univalent and colourless ion. According to Grimm and Sommerfeld (*loc. cit.*) the removal of an electron from the eighteen group requires at least 40,000 calories more (per gram-ion) with Ag^+ than with Cu^+.

In the next (rare earth) period the relations are more complicated. We start with Xe 54 = (2) (8) (18) (18) (8), and three processes occur during the period, the development of the fourth quantum group from 18 to 32, of the fifth from 8 to 18, and the formation of a new sixth quantum group of 8. We begin as before with the establishment of the N_{11} pair in the sixth group (Cs 55, Ba 56): then the fifth quantum group of 8 opens: La 57 = (2) (8) (18) (18) (2, 6, 1) 2. With the next atom Ce 58 the fourth group opens, giving (2) (8) (18) (2, 6, 10, 1) (2, 6, 1) 2. In the succeeding elements the new electrons all go to this 4_4 subgroup, until it is completely filled at Lu 71 = (2) (8) (18) (2, 6, 10, 14) (2, 6, 1) 2. Throughout the whole of this series of rare earth metals, from La 57 to Lu 71, the fifth and sixth quantum groups remain unchanged at (2, 6, 1) 2: the only change of structure is the growth of the 4_4 subgroup of 14 ($6 \times 4_{43} + 8 \times 4_{44}$). There is thus a very close similarity of properties (since the only change is far down in the atom), such as we find nowhere else in the table. The elements are all trivalent, giving an ion $-$ (2, 6). It is however to be noticed that as the first occupants of a new type of orbit are usually more easily removed than the later ones, Ce 58, which has one 4_4 electron, can lose this and become quadrivalent, and Pr 59, which has two, can lose one of them in the same way, though less easily than cerium.

The ions of the rare earth metals are paramagnetic (some very highly) and coloured. The colour is of quite a different type to that of the transition elements of the two preceding periods: instead of broad bands of several hundred Å.U. the solutions give narrow absorption bands or lines, often not exceeding 10 Å.U. in breadth. This is strong evidence in favour of Bohr's view that the developing group in these elements is far down in

the atom. The broadening of the absorption lines of an ion in solution is due to the electric fields of neighbouring atoms, which break up each line into components, whose separation depends on the strength of the field (Stark effect) : as the different ions present are thus affected in various degrees, the result is to spread the sharp line into a band. The broadening will obviously be greater, the more the orbits in question are exposed to the fields of neighbouring atoms; and hence it is less in the rare earth metals, where these orbits are in an inner group, shielded from the influence of other atoms, than in the previous periods, in which the imperfect quantum group is the outermost group of the ion.

In lutecium (71) the fourth quantum group is full, and hence in hafnium (72) the new electron must go to the fifth group, giving the structure—(32) (2, 6, 2) 2. Thus if the theory is sound, the trivalent rare earth metals should stop at 71, and 72 should be an element of the fourth periodic group, with a valency of four. If this were not so, it would mean that the whole scheme was at fault ; and it would be a unique case of a rise of valency of two units in going from one element to the next (from 72 to quinquevalent tantalum 73), indicating that an electron became less firmly bound when the nuclear charge increased, whereas the reverse must always happen. Hence the importance attached to determining whether 72 was a rare earth (trivalent) element or an analogue of zirconium : it was ultimately proved to have an extraordinarily close similarity to zirconium. In the following elements (Ta, W, Re, Os, Ir, Pt) we have the same kind of development as in the transition elements of the two long periods : but the work of Sommer and others indicates that the resemblance is to the first rather than the second of these (V–Ni and not Nb–Pd), and that these elements have two electrons in the outer quantum group. This is supported by the behaviour of gold, in which, as in copper but not silver, some of the electrons of the penultimate 18 group can be utilized as valency electrons. Why this should be true of two electrons in gold and only one in copper—in other words, why copper has valencies of one and two, and gold of one and three—is not yet known.

In the elements from gold (79) to emanation (86) we have the normal type of growth of the outer group of eight. All the elements after mercury (80) have radioactive isotopes, and after bismuth (83) all the isotopes are radioactive. Hence the absence of elements 85 (eka-iodine) and 87 (eka-caesium) is probably due to instability of the nucleus.

The last period (Ra, Ac, Th, Pa, U) might be expected to be parallel to the rare earth period, the fifth group beginning to develop at 90 (Th). It is clear however from their properties, and especially from the continuous increase of valency up to the last member, that this is not so; if it were the increase would cease (as it does with cerium) when the expansion of the 18 group began. These elements must resemble the first or second long period, and all the electrons added after emanation must go to the sixth or seventh quantum group. The first two electrons (in Ra) will clearly go to the seventh. Whether in Ac–U we have as in the first long period two, or as apparently in the second, only one electron in the outermost group, is uncertain, as the spectra of these elements have not yet been worked out. Sommer (*loc. cit.*) considers it probable, on the analogy of the earlier periods, that there is only one.

To sum up the results of this physical investigation it will be seen that Bohr recognizes four different types of atoms.

1. Those in which all the electronic groups are complete (this word being applied to the subordinate stable numbers such as 8 and 18, as well as to the absolutely complete numbers of $2n^2$). These elements form no compounds: they are the inert gases.

2. Those in which all but the highest quantum group are complete. These include the first two short periods, the elements up to seven places before and two after each inert gas, and generally all those which are not included in frames in the Bohr periodic table, p. 39. These elements have a fixed number of valency electrons,[1] and their simple ions are colourless.

3. Those in which the two outermost electronic groups are imperfect (in the wider sense given above under (1)): these are enclosed in a single frame. They show valencies varying by single units, are markedly catalytic, and form coloured and paramagnetic ions. These may conveniently be called the transition elements; this term has commonly been limited to the triads with which each series concludes, but now that we recognize that these triads are not peculiar, but are only the final stages of a process extending over the preceding elements as well, the designation may be extended to the whole series.

[1] This does not necessarily mean that the value of the valency as ordinarily expressed is constant; but it implies that this value, properly understood, normally changes only by 2 units at a time. The ' proper understanding ' of these relations is the main object of the succeeding chapters, in which certain real and apparent exceptions to the ' even number rule ' are discussed.

4. Those in which the three outermost groups are imperfect (double frame); these are the rare earth metals. They resemble class 3 in some respects (especially in colour, paramagnetism, and catalytic power), but are unique in constituting a long series of elements all of the same valency, and all very similar in properties.

The list of atomic structures on pp. 48–50 summarizes the results of these investigations, in accordance with the latest spectroscopic data: I am much indebted to Dr. E. C. Stoner for help in compiling this.[1] It cannot be regarded as final, since some of the details, especially as to the number of electrons in the highest quantum group in the transitional elements, are still

[1] For the recent developments of the theory relating the structure to the spectral terms, see Heisenberg, *Z. f. Phys.* 1925, **32**, 841; Hund, ibid. **33**, 345; R. H. Fowler and Hartree, *Proc. Roy. Soc.* 1926, **111**, 83. A clear and comparatively simple account of the theory is given in Sommerfeld's *Three Lectures on Atomic Physics* (Methuen, 1926). For its application to particular elements see Grimm and Sommerfeld, *Z. f. Phys.* 1926, **36**, **36**; Sommer, ibid. **37**, 1; Laporte, *J. Opt. Soc. Amer.* 1926, **13**, 1. McLennan, McLay, and H. G. Smith *(Proc. Roy. Soc.* 1926, **112**, 76) give a complete list, based on the work of Heisenberg and Hund; this agrees with the Table in nearly every case: but for each of the elements Re, Os, Ir, Pt, for which the spectra have not been fully worked out, they also suggest alternative formulae. For each of the last three elements (Th, Pa, U) they give two alternative formulae, neither of which is that in the Table: in the first of these it is supposed that the expansion of the fifth quantum group of 18 may have begun, which would make these elements analogous to the rare earths, a view which their chemical behaviour does not seem to support.

These alternative suggestions of McLennan, McLay, and Grayson are as follows (the first four quantum groups are completely filled in all these elements).

		5_{11}	5_{21} 5_{22}	5_{32} 5_{33}	5_{43} 5_{44}	6_{11}	6_{21} 6_{22}	6_{32} 6_{33}	7_{11}
75 Re	(60)	2	2 4	6		1			
76 Os	(60)	2	2 4	7		1			
77 Ir	(60)	2	2 4	8		1			
78 Pt	(60)	2	2 4	9		1			
Pt	(60)	2	2 4	4 6					
..	..	..	..	..	..	..	..	..	..
90 Th	(60)	2	2 4	4 6	1	2	2 4	1	2
Th	(60)	2	2 4	4 6		2	2 4	2	2
91 Pa	(60)	2	2 4	4 6	2	2	2 4	1	2
Pa	(60)	2	2 4	4 6		2	2 4	3	2
92 U	(60)	2	2 4	4 6	3	2	2 4	1	2
U	(60)	2	2 4	4 6		2	2 4	4	2

in doubt. But a comparison of this with earlier lists, such for example, as that given by Coster in 1923,[1] shows that the development of the theory has not seriously affected the essential conclusions, except in the distribution of the electrons of a group among the subgroups. Where the structure of an element is still in doubt, this is usually because the energies of the two alternative orbits do not greatly differ, and hence the doubt is of less importance in interpreting the chemical behaviour of the element, which depends on the energy of these orbits. It must of course be remembered that the structure given for an element in the table is that of a ' normal ' atom, as Bohr calls it, that is, of an isolated atom of the element, at a temperature low enough for it not to radiate energy, and to have its electrons in the most stable orbits possible. With some elements such ' normal ' atoms can scarcely be said to exist at all, except transiently in a discharge tube—as for example with carbon, where the atoms remain combined up to temperatures at which some of the electrons must be far from their ' normal ' orbits. In such cases the finer details of the structure may be of less chemical interest ; but nevertheless a knowledge of the normal structure often gives us much information as to the chemical behaviour of the element, even when the normal atom is highly unstable. Thus the probable structure (on the spectroscopic evidence) of the normal palladium atom, which is that of a quasi-inert gas (2) (8) (18) (18), cannot apply to the element as we know it in the solid state : its metallic character shows that the fourth quantum group has been broken into, and that the solid, like all other metals, contains free electrons ; and the chemical evidence leads to the same conclusion. But the greater stability of the 18 group in this transition series as compared with the one before and the one after (which is what the structure of the normal palladium atom indicates), is clearly reflected in the chemical behaviour of the neighbouring elements, especially, as we have seen, in that of silver as compared with copper and gold.

[1] *Naturwissenschaften*, **11**, 571.

n =	1	2		3			4			
k_j =	1_1	1_1	$2_1\ 2_2$	1_1	$2_1\ 2_2$	$3_2\ 3_3$	1_1	$2_1\ 2_2$	$3_2\ 3_3$	$4_3\ 4_4$
1 H	1									
2 He	2									
3 Li	2	1								
4 Be	2	2								
5 B	2	2	1							
6 C	2	2	2							
7 N	2	2	3							
8 O	2	2	4							
9 F	2	2	5							
10 Ne	2	2	2 4							
11 Na	2	2	2 4	1						
12 Mg	2	2	2 4	2						
13 Al	2	2	2 4	2	1					
14 Si	2	2	2 4	2	2					
15 P	2	2	2 4	2	3					
16 S	2	2	2 4	2	4					
17 Cl	2	2	2 4	2	5					
18 A	2	2	2 4	2	2 4					
19 K	2	2	2 4	2	2 4		1			
20 Ca	2	2	2 4	2	2 4		2			
21 Sc	2	2	2 4	2	2 4	1	2			
22 Ti	2	2	2 4	2	2 4	2	2			
23 V	2	2	2 4	2	2 4	3	2			
24 Cr	2	2	2 4	2	2 4	5	1			
25 Mn	2	2	2 4	2	2 4	5	2			
26 Fe	2	2	2 4	2	2 4	6	2			
27 Co	2	2	2 4	2	2 4	7	2			
28 Ni	2	2	2 4	2	2 4	8	2			
29 Cu	2	2	2 4	2	2 4	4 6	1			
30 Zn	2	2	2 4	2	2 4	4 6	2			
31 Ga	2	2	2 4	2	2 4	4 6	2	1		
32 Ge	2	2	2 4	2	2 4	4 6	2	2		
33 As	2	2	2 4	2	2 4	4 6	2	3		
34 Se	2	2	2 4	2	2 4	4 6	2	4		
35 Br	2	2	2 4	2	2 4	4 6	2	5		
36 Kr	2	2	2 4	2	2 4	4 6	2	2 4		

ATOMIC STRUCTURES (2)

n =	1	2	3	4					5				6
k_j =	–	–	–	1_1	2_1 2_2	3_2 3_3	4_3 4_4		1_1	2_1 2_2	3_2 3_3		1_1
37 Rb	2	8	18	2	2 4				1				
38 Sr	2	8	18	2	2 4				2				
39 Y	2	8	18	2	2 4	1			2				
40 Zr	2	8	18	2	2 4	2			2				
41 Nb	2	8	18	2	2 4	4			1				
42 Mo	2	8	18	2	2 4	5			1				
43 Ma	2	8	18	2	2 4	6			1				
44 Ru	2	8	18	2	2 4	7			1				
45 Rh	2	8	18	2	2 4	8			1				
46 Pd	2	8	18	2	2 4	4 6			–				
47 Ag	2	8	18	2	2 4	4 6			1				
48 Cd	2	8	18	2	2 4	4 6			2				
49 In	2	8	18	2	2 4	4 6			2	1			
50 Sn	2	8	18	2	2 4	4 6			2	2			
51 Sb	2	8	18	2	2 4	4 6			2	3			
52 Te	2	8	18	2	2 4	4 6			2	4			
53 I	2	8	18	2	2 4	4 6			2	5			
54 X	2	8	18	2	2 4	4 6			2	2 4			
55 Cs	2	8	18	2	2 4	4 6			2	2 4			1
56 Ba	2	8	18	2	2 4	4 6			2	2 4			2
57 La	2	8	18	2	2 4	4 6			2	2 4	1		2
58 Ce	2	8	18	2	2 4	4 6	1		2	2 4	1		2
59 Pr	2	8	18	2	2 4	4 6	2		2	2 4	1		2
60 Nd	2	8	18	2	2 4	4 6	3		2	2 4	1		2
61 Il	2	8	18	2	2 4	4 6	4		2	2 4	1		2
62 Sm	2	8	18	2	2 4	4 6	5		2	2 4	1		2
63 Eu	2	8	18	2	2 4	4 6	6		2	2 4	1		2
64 Gd	2	8	18	2	2 4	4 6	7		2	2 4	1		2
65 Tb	2	8	18	2	2 4	4 6	8		2	2 4	1		2
66 Ds	2	8	18	2	2 4	4 6	9		2	2 4	1		2
67 Ho	2	8	18	2	2 4	4 6	10		2	2 4	1		2
68 Er	2	8	18	2	2 4	4 6	11		2	2 4	1		2
69 Tm	2	8	18	2	2 4	4 6	12		2	2 4	1		2
70 Yb	2	8	18	2	2 4	4 6	13		2	2 4	1		2
71 Lu	2	8	18	2	2 4	4 6	6 8		2	2 4	1		2
72 Hf	2	8	18	2	2 4	4 6	6 8		2	2 4	2		2

ATOMIC STRUCTURES (3)

n =	1	2	3	4	5			6			7
k_j =	–	–	–	–	1_1	2_1 2_2	3_2 3_3	1_1	2_1 2_2	3_2 3_3	1_1
73 Ta	2	8	18	32	2	2 4	3	2			
74 W	2	8	18	32	2	2 4	4	2			
75 Re	2	8	18	32	2	2 4	5	2			
76 Os	2	8	18	32	2	2 4	6	2			
77 Ir	2	8	18	32	2	2 4	7	2			
78 Pt	2	8	18	32	2	2 4	8	2			
79 Au	2	8	18	32	2	2 4	4 6	1			
80 Hg	2	8	18	32	2	2 4	4 6	2			
81 Tl	2	8	18	32	2	2 4	4 6	2	1		
82 Pb	2	8	18	32	2	2 4	4 6	2	2		
83 Bi	2	8	18	32	2	2 4	4 6	2	3		
84 Po	2	8	18	32	2	2 4	4 6	2	4		
85 —	2	8	18	32	2	2 4	4 6	2	5		
86 Em	2	8	18	32	2	2 4	4 6	2	2 4		
87 —	2	8	18	32	2	2 4	4 6	2	2 4		1
88 Ra	2	8	18	32	2	2 4	4 6	2	2 4		2
89 Ac	2	8	18	32	2	2 4	4 6	2	2 4	1	2
90 Th	2	8	18	32	2	2 4	4 6	2	2 4	3	1
91 Pa	2	8	18	32	2	2 4	4 6	2	2 4	4	1
92 U	2	8	18	32	2	2 4	4 6	2	2 4	5	1

IV

VALENCY: FUNDAMENTAL PRINCIPLES

VALENCY is a general term used to describe the power which atoms possess of combining with one another to form molecules. Our object is to explain this power in terms of atomic structure, that is, to discover the electronic mechanism by which atoms are held together, and to show how the variation of valency from one atom to another is related to the arrangements of the electrons in these atoms. We must therefore first consider what we can learn of the nature of valency from the chemical evidence.

The earliest serious theory of valency was that of Berzelius (1812), who assumed that the force between atoms was purely electrostatic, that the molecule of sodium chloride, for example, was held together by the attraction of a positive charge on the sodium and a negative charge on the chlorine. This theory, which was strongly supported by the phenomena of electrolysis, was overthrown as a universal theory of valency about 1840 from its inability to account for certain facts of organic chemistry, especially the replacement of positive hydrogen by negative chlorine without any fundamental change in the properties of the molecule (Dumas, 1834). The rival theory, that of structural chemistry, made no assumptions as to the nature of the force between the atoms, but regarded it as essentially non-polar, that is, as not involving any opposite character in the two linked atoms. The enormous success of this theory in the sphere of the carbon compounds rather obscured the fact that the electrical theory of Berzelius still remained quite satisfactory if it was confined to the linkages between oppositely charged ions in a salt. In 1869 it was pointed out by Mendeléeff, in his original formulation of the Periodic Law, that the numerical value of the valency is closely related to the periodic groups, and normally changes by one unit when we pass from one group to the next.

With the rise of the Arrhenius theory of electrolytic dissociation in and after 1887 the views of Berzelius again came to the front, and it became clear that atomic linkages are of two kinds, one ionizable and presumably due to electrostatic attraction, and the other non-ionizable, and not explicable in this simple way; but this distinction was not much regarded, mainly because the

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investigation of the two kinds of linkage fell into different hands, those of the organic and those of the inorganic chemist.

Meanwhile examples were accumulating of compounds which did not seem to fit in with either of these two theories, and especially of instances in which two or more apparently saturated molecules combine to form complex molecules of greater or less stability. These were for some time shelved under the convenient name of molecular compounds, but in 1892 Alfred Werner put forward a new theory to account for them : in this theory, which was based on a great mass of evidence, he practically assumed a new force, called co-ordination, which was free from the limitations of the ordinary valency (and in particular was independent of the periodic group to which an atom belongs), but was subject to other limitations of its own. This new theory was not very seriously regarded by chemists in general until in 1911 it enabled its author to predict the occurrence of optical activity in certain metallic compounds, and to verify his predictions by experiment. It then became recognized that the co-ordination theory was as successful in its own sphere as the structural theory was in organic chemistry, although the two appeared irreconcilable with one another.

In general then it may be said that the chemical evidence points to the existence of three kinds of linkage between the atoms in a molecule :

(1) Polar or ionizable linkages between the oppositely charged ions of a salt.

(2) Non-polar non-ionizable linkages, especially prevalent in organic compounds.

(3) The co-ordinate links of Werner, capable of uniting apparently saturated molecules ; the number of these links is not determined, as those of (1) and (2) are, by the group in the periodic table to which the element belongs.

This is in outline the chemical statement of the fundamental problems of valency which the physicist is called upon to explain by his theory of atomic structure.

As soon as the existence of electrons as a universal constituent of all atoms was recognized, attempts were made to utilize them to provide a mechanism for chemical combination. J. J. Thomson early suggested that the molecule might be held together by the electrostatic force resulting from a migration of an electron from one atom to another.

Drude in 1904 made a suggestion which comes very near to

our modern ideas. In that year Abegg [1] formulated his ' rule of 8 '. This was a development of Mendeléeff's relation between the valency of an element and its periodic group. Abegg ascribed to every element positive and negative valencies, the former being exhibited, for example, in its compounds with the halogens, the latter in those with hydrogen. He sums up his conclusions thus : ' Every element has both a positive and a negative maximum valency, the sum of which is always 8, and the former corresponds to the group-number.' Thus he gives the table :

Group	1	2	3	4	5	6	7
Normal valency	+1	+2	+3	+4	−3	−2	−1
Contra-valency	(−7)	(−6)	(−5)	—	+5	+6	+7

Drude [2] makes this comment : ' Abegg's positive valency number v, whether it is a normal or a contra-valency, signifies the number of loosely attached negative electrons in the atom : his negative valency number v^1 means that the atom has the power of removing v^1 negative electrons from other atoms, or at least of attaching them more firmly to itself.' Considering the time when this was written, it shows a very remarkable advance on current theories, and suggests that but for his untimely death Drude might have anticipated much of the later development of the theory by some ten years. A somewhat detailed physical theory of valency, especially of non-polar compounds, was proposed by Stark,[3] but as this was founded on Thomson's original suggestion of a uniform sphere of positive electrification in the atom, it did not survive the establishment of the Rutherford atom.

No very definite relation between valency and structure could however be reached until after the enunciation of the theory of atomic number in 1913, and the determination of the values of these numbers for the different elements. This gave the number of electrons in each atom, and indicated that the numbers found in the inert gases were capable of a peculiarly stable arrangement. The first definite hypotheses as to the mechanism underlying valency, and the relation of this property to the atomic number, were put forward independently in 1916 by Kossel and by G. N. Lewis, the former dealing with polar and the latter with non-polar linkages.

[1] *Z. anorg. Chem.* 1904, **39**, 343.
[2] *Ann. d. Phys.* 1904, **14**, 722.
[3] Summarized in his *Prinzipien der Atomdynamik*, Bd. III, Leipzig, 1915.

Kossel[1] pointed out that the element next before an inert gas is always a strongly electronegative and univalent halogen, and that immediately following an equally strongly electropositive and univalent alkali metal: that the element next before the halogen is negative and divalent, and that next following the alkali metal positive and divalent, and so on: and that these facts could be simply explained by supposing that the inert gas had a stable arrangement of electrons which the other elements strove to attain by acquiring or losing the necessary number of electrons. For example, in the series

S	Cl	A	K	Ca
16	17	18	19	20

eighteen electrons must be capable of a stable arrangement (since argon, in which this number occurs, is inactive), and this arrangement chlorine could assume by taking up one, and sulphur by taking up two electrons: while potassium could do the same by losing one and calcium by losing two. This would give the stable ions (all with eighteen electrons) S^{--}, Cl^{-}, K^{+}, Ca^{++}, which by combination would yield the neutral salts K_2S, KCl, $CaCl_2$, &c., in which the electronegative part had gained the necessary electrons at the expense of the electropositive part, the ions in the salt being held together by the electrostatic forces so produced. On this theory it appears that the valency of an atom is the number of electrons it must gain (if electronegative) or lose (if electropositive) in order to have a total number capable of forming a stable arrangement.

Kossel points out that the existence of ions with these charges can be proved by physico-chemical methods for all elements one or two places from an inert gas, and claims that similar ions can be assumed by analogy to exist with more remote elements (as in NH_3 and PH_3), though he admits that with them the tendency to ionize is less. These simple relations break down when we come to the elements near the middle of the long periods (transition elements in the wider sense), but they still hold for the neighbours of the inert gases in every period. He illustrates his theory by a diagram in which the actual number of electrons in the ion is plotted against the atomic number, and shows that if we interpret valency in his way, the actual number tends to be that of the nearest inert gas.

This theory is based upon atomic number, but it does not

[1] *Ann. d. Phys.* 1916, **49**, 229.

involve the acceptance of any particular atomic model : it only assumes that some of the electrons are firmly held and unaffected by external influences, while there are others loosely bound, which are active in chemical combination, as they are in producing the optical spectra. (It will be noticed that Drude had very nearly arrived at this view twelve years earlier, though he could not assign specific numbers of electrons to the atoms.)

Kossel's theory explains the connexion between the valency of an element and its position in relation to the inert gases. It accounts for the peculiar characteristic of the chemical link that it satisfies one unit of combining power of each of the atoms concerned, and it is in complete agreement with the results of the electrolytic theory. Further support has since been given to it by the results of spectroscopy and of the X-ray examination of crystals. On all these grounds its truth cannot be doubted, so far as a particular class of compounds is concerned. It is the essence of the theory that the two linked atoms should be dissimilar in character, one tending to lose and the other to gain electrons.

But there are many molecules in which it is difficult or impossible to say which is the positive and which the negative atom, such as sulphur dioxide, carbon dioxide, or still more strikingly the diatomic elementary gases like hydrogen, oxygen, nitrogen, and chlorine. There is no reason to think that in hydrogen, for example, either atom has lost an electron to the other. Nor do such compounds or elements ionize in solution. The existence of two kinds of linkage, ionized and non-ionized, had been apparent from the time of the overthrow of the Berzelius theory, and had been made still more evident by the work of Arrhenius and van't Hoff ; and it was clear that Kossel's theory of electronic transference, while it was quite satisfactory as an explanation of the ionized link between dissimilar atoms, was entirely incapable of accounting for non-ionized links between similar atoms : this was indeed recognized by Kossel himself. The problem is not merely to discover a mechanism by which atoms can be united without the transference of electrons, but also to explain why the numerical value of the valency is the same, at any rate in simple instances, for both kinds of linkage. Thus hydrogen and chlorine are univalent, and oxygen is divalent, whether they are combined with carbon, or with metals, or with one another, and whether the resulting molecules are ionized or not.

The solution was given in the same year (1916) by G. N. Lewis.[1] He assumed, like Kossel, that the cause of chemical combination is the tendency of the electrons to redistribute themselves among the atoms so as to form more stable arrangements such as occur in the inert gases; but he made an advance of fundamental importance by suggesting that it was possible for an electron to be shared between two atoms so that in some way it could count towards the stability of both. How this sharing was effected he did not discuss: in fact with his static model (the 'cubic atom') this question did not arise, since the existence of such an atom could not in any case be explained without the assumption of unknown forces. With a dynamic model such as we now accept, the question becomes of great importance, though it can only be very imperfectly answered in the present state of our knowledge. For our immediate purpose, however, it need not be discussed: if we assume that such sharing is in some way possible, so that each electron enters into the constitution of both atoms, we can at once account for the valency of atoms in their non-ionized compounds. Chlorine, for example, has one electron less than the stable number of 18. Hence, as we have seen, it readily takes up an electron from an atom that readily loses one, such as sodium, to form a chlorine ion with a negative charge. But it can also complete its number of electrons by sharing one belonging, say, to another chlorine atom; and if at the same time the second chlorine atom shares another electron belonging originally to the first, then each is satisfied. The various states of the atom are shown below, the dots and crosses representing valency electrons, without any assumption as to their positions in space: in the atomic symbols beneath, the shared electrons are underlined:

Cl = (2)(8)(7) $[Cl]^-$ = (2)(8)(8) $-Cl$ = (2)(8)(6, <u>2</u>)

The Kossel method of linkage is primarily confined to compounds between elements of opposite character: it enables an atom that has too many electrons for stability to give up the excess to atoms that have too few. The Lewis method, on the other hand, enables a smaller number of electrons to do the work of a larger: it is essentially a linkage for atoms each of which is

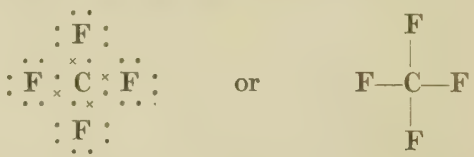
[1] *J. Amer. Chem. Soc.* 1916, **38**, 762.

a few electrons short of a stable number, i.e. for electronegative atoms. This entirely agrees with experience. Non-ionized compounds are far commoner among electronegative elements : they are comparatively rare among the metals. To distinguish these two forms of linkage Langmuir suggested the very convenient terms ' covalency ' and ' electrovalency ', which have been generally adopted.

Another conclusion of fundamental importance is that the numerical value of the valency is the same on both theories. The electrovalency of Kossel is equal for a negative element to the number of electrons that it needs to make up a stable number. Since on the Lewis theory it gains an electron for each covalency that it forms, the number of covalencies must be equal to this defect, and so to the electrovalency. For a positive element, the electrovalency is equal to the number of electrons in excess of a stable number. On the Lewis theory the atom in forming a covalency must not only share an electron belonging to the other atom, but also give to the other atom a share in one of its own electrons, and therefore the number of such links which it can form cannot exceed the number of electrons which it has to offer, so that here also the covalency and the electrovalency are numerically equal. Thus we can see why chlorine is univalent in methyl chloride as well as in sodium chloride, and zinc divalent in zinc methide as well as in zinc sulphate.

The necessity of two shared electrons to every covalent link is an essential part of the Lewis theory ; and as this assumption has been questioned, its justification must be considered. The most fundamental conclusion of the chemical study of valency, quite apart from any question as to its mechanism, is that every link, whether ionized or not, satisfies one unit of combining power of *each* of the two atoms which it unites. The single link between the sodium and the chlorine in sodium chloride satisfies both the single valency of the sodium and that of the chlorine : when carbon with four valencies unites with four hydrogen atoms which have one each, four links are formed, each of which satisfies one unit for the hydrogen and one for the carbon. The process is analogous to the linking of two hooks, one for each atom, and not to the hanging of a series of hooks from a ring. Any proposed mechanism of valency must take account of this fact. The Kossel theory does so, because on that theory the electron lost by one atom must be taken up by the other, since the whole molecule is electrically neutral. The Lewis theory only does so

if with Lewis we make the additional assumption that every covalency requires two electrons to be shared between the two atoms. For example, fluorine is univalent: its structure is (2)(7), and so is one electron short of the stable number of neon, (2)(8). It can make up this defect in combination with sodium, by taking the loose electron from a sodium atom. It can combine with carbon (2)(4), which has four valency electrons, and also is four short of the neon number, by four fluorine atoms each sharing one of the valency electrons of the carbon. This gives each fluorine atom the extra electron which it needs. But we know that in this combination the carbon also is satisfied, so that it must have acquired four electrons in addition to the four which it had originally, and which it can still use although it has shared them with the fluorines. This means that every time it makes a link by sharing one of its own electrons with a fluorine atom, it also shares one of the electrons belonging to the fluorine: a link is formed with each fluorine, consisting of a shared electron from the carbon and one from the fluorine, so that the carbon, as well as the four fluorines, has its valency electrons made up to eight, the compound being written



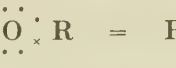
We shall see later (p. 102) that there is evidence showing that in a small number of unstable compounds hydrogen can be attached to one of the lighter atoms by a covalent link formed of a single shared electron: but such links are exceptional. In all ordinary compounds two electrons are required; indeed, if it were not so, one atom might satisfy the affinity of another without satisfying its own, or limiting its power of combination with further atoms.

Thus the theories of Kossel and of Lewis provide an electronic mechanism for the two kinds of linkage, polar and non-polar, which the chemical evidence requires. So far they make little change in the accepted structural formulae. We distinguish the ionized links by Werner's device of the square brackets enclosing the non-ionizably attached atoms of a polyatomic ion, and with the non-ionizable links themselves we merely substitute two dots for a line. We then find (at any rate for the normal

compounds of the lighter elements) that hydrogen, unless it is ionized, always has two electrons, and the other atoms are each provided with eight electrons, shared or unshared. But in the same paper Lewis makes a further suggestion, which has subsequently been shown to explain the co-ordination compounds of Werner. He says :[1] ' While the two dots of our formulae ' (indicating two shared electrons) ' correspond to the line which has been used to represent the single bond, we are led through their use to certain formulae of great significance which I presume would not occur to any one using the ordinary symbols. Thus it has been generally assumed that what is known as a bivalent element must be tied by two bonds to another element or elements, or remain with an " unsaturated valence ". On the other hand we may now write formulae in which an atom of oxygen is tied by only one pair of electrons to another atom, and yet have every element in the compound completely saturated. To illustrate this important point we may write the formulae of perchlorate, sulphate, orthophosphate, and orthosilicate ions, in which each atom has a complete shell of eight electrons. Thus

represents all of these ions. If X is chlorine, the ion has one negative charge : if sulphur, it has two negative charges, and so on.'

The full significance of this conception will be apparent later, but the fundamental idea is simple. A divalent atom like oxygen needs two more valency electrons. It can gain these by forming two covalent links, that is, by sharing two electrons belonging to another atom or atoms, while at the same time the other atom or atoms share two belonging to the oxygen



This is the usual divalent oxygen of structural chemistry. The new mode of combination which Lewis suggests is that the oxygen only forms a single covalency—only shares two electrons

[1] *Loc. cit.* p. 778.

with the other atom—but that both of these electrons come from the other atom

This constitutes only a single link, but it increases the valency electrons of the oxygen by two, and therefore the oxygen becomes saturated. In other words, he suggests that the two shared electrons which constitute a covalency can arise in two ways: (1) as they normally do, by each of the atoms concerned contributing one of them; or (2) by one of the atoms contributing both. The application of this idea to the oxy-acids of the type H_nXO_4 is clear. The eight shared electrons in the ion

are all needed to make up the valency groups of the four oxygens from six to eight; hence they are not derived from the oxygens, but either from the central atom X or from outside, and every electron coming from outside must give the molecule a negative charge. If X is chlorine, with seven electrons to start with, it will need one more, giving the univalent ion $[ClO_4]'$: if it is sulphur, with six, it will need two more, giving $[SO_4]''$: in the same way phosphorus will need three and silicon four, so that we arrive at the familiar formulae $HClO_4$, H_2SO_4, H_3PO_4, H_4SiO_4.

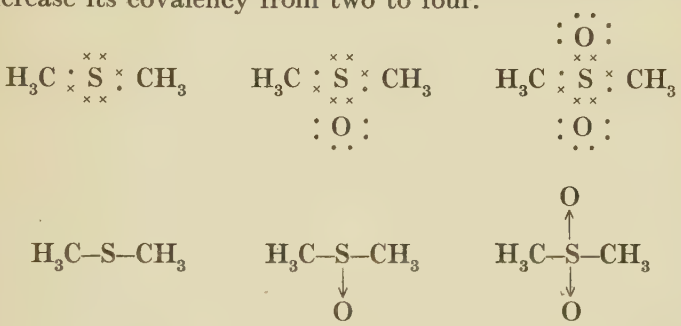
This new type of covalency needs a name and a symbol. It may be called a co-ordinate link, since it affords, as will be shown later, an explanation of the co-ordination compounds of Werner; and it may be expressed in formulae by an arrow (in place of a line) pointing away from the atom which contributes the two electrons: [1]

Normal Covalency.

Co-ordinate Covalency.

[1] This is the 'semi-polar' link of Sugden and others, which is also written $\overset{+}{A}-\overset{-}{B}$ or $A \rightleftharpoons B$. See further Chapter VII.

In forming co-ordinate links an atom will obviously not be subject to the same limitations (according to its periodic group) as in forming normal links. Sulphur, for example, can as a rule only form two normal covalencies, as in $(CH_3)_2S$, because these give it the full valency group of eight. Of these eight, two pairs are shared with the two carbon atoms, while the other four are not shared, and form what the Americans call ' lone pairs '. But though the sulphur atom in $(CH_3)_2S$ is in this sense saturated, it can form two more covalencies of the second type, by sharing these lone pairs with atoms, for example, of oxygen, which need two electrons to make up their full complement. Thus the possibility of co-ordination enables the sulphur atom to increase its covalency from two to four.



We thus arrive at a mechanism for the three types of linkage which as we have seen (p. 52) the chemical evidence shows to exist.

(1) Polar or ionized linkages : due to the transference of electrons from one atom to another (electrovalency).

(2) Non-polar, non-ionizable (covalent) linkages : due to the sharing of electrons, two to each link, between the atoms. These can arise in two ways :

(*a*) One electron contributed by each atom : normal covalencies : limited in number (like electrovalencies) by the periodic group of the atom.

(*b*) Both electrons contributed by the same atom : co-ordinate covalencies ; when these are formed the numerical value of the covalency is no longer dependent on the periodic group to which the atom belongs.

So much for the electronic mechanism of the linkages themselves. The reason for their formation is that they produce more stable groups of electrons than the isolated atoms possess, groups such as are found in the inert gases. Now with the exception of

helium, which has a single group of two electrons, all the inert gases have been shown to have an outer group of eight. It was therefore originally assumed that the redistribution of electrons in chemical combination led to the production of a valency group of eight with all atoms except the immediate neighbours of helium (hydrogen, lithium, beryllium), where the number was two. This was the foundation of the octet theory of Lewis, first published in 1916 (*loc. cit.*) and subsequently developed by himself, Langmuir, and others. The progress of physics has shown that the static atom must be given up, and with it the spatial relations involved in the cubic octet. But it is still true that in a very large number of compounds the stability of atoms is determined by their having a group of eight valency electrons : so that the octet, regarded simply as a number of electrons, retains its importance for many purposes. If we assume that it represents the maximum number possible in a valency group, and at the same time accept Lewis's theory that two electrons are required to form a covalency, we must conclude that the largest number of covalent links that any atom can form is four. The compounds of the elements of the first short period (down to fluorine) support this view. But in the second short period (Na 11 to Cl 17) we meet with a serious difficulty in sulphur hexafluoride SF_6. This is a gas (boiling below -50°) of quite extraordinary stability. It can be passed through water or even hot potash solution without change : it is not acted on by sodium below a red heat. These properties make it clear that it is not a salt, but a covalent compound like carbon tetrafluoride. Since we never find two fluorine atoms joined together (except in elementary fluorine) all the six fluorine atoms must be attached by covalent links to the sulphur. If each link consists of two shared electrons, the whole valency group must contain twelve. The sulphur atom is obviously suited to form such a compound, since it has six valency electrons to offer for the six links. The links cannot be formed of single electrons, because such links must be (and are always found to be) very weak, whereas the stability of sulphur hexafluoride is abnormally great. A further examination of the compounds of the heavier elements shows that this is no isolated case, but is one of many : for example, in addition to the numerous other hexafluorides, all Werner's optically active compounds of chromium, cobalt, and other metals belong to this category.

We must therefore conclude (as Lewis himself subsequently

did) that the valency group is not limited to eight, but can with some atoms rise to twelve. Even this is not the maximum, for we find a volatile octofluoride of osmium OsF_8 in which we must assume a valency group of sixteen electrons.

Before we go on to discuss in more detail the criteria of the different forms of linkage and the conditions of their stability, it will be useful to consider the application of these fundamental ideas to some of the simpler and more familiar types of compound, taken mainly from the first short period of Mendeléeff.

Periodic group	1	2	3	4	5	6	7	
Element	(H 1)							(He 2)
	Li	Be	B	C	N	O	F	Ne
Atomic number	3	4	5	6	7	8	9	10
Valency electrons	1	2	3	4	5	6	7	(8)

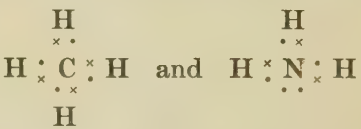
All these elements from lithium onwards have an inner (1-quantum) group of two electrons, and hence their number of valency electrons is two less than the atomic number, and is of course equal to the group number in the periodic table. It is convenient to distinguish those electronic groups which are not affected in chemical combination as the *core* of the atom, in contrast to the outer group of valency electrons which is modified in combination : thus in all these elements after hydrogen there is a core of two. The ' stable arrangements ' to which all these elements tend in their compounds are those of the inert gases helium (2) and neon (2) (8).

On these principles we can answer the much disputed question whether hydrogen should be regarded as belonging to the alkali metals or to the halogens : it clearly has properties in common with each class. The alkali metals are typical univalent metals ; they have one electron more than an inert gas, and this electron is therefore easily lost. Hydrogen, consisting of a nucleus of one proton with a single attendant electron, also loses this electron easily, leaving the proton—that is, the hydrogen ion—behind. In this respect it is like an alkali metal. The halogens, on the other hand, are typical univalent electronegative elements, having one electron less than an inert gas, and so very ready to take one up, either by transference to give a univalent anion, or by sharing, as in fluorine gas or methyl fluoride. Hydrogen, while it has one electron more than a proton, has one less than helium, and so it readily takes one up, just as a halogen does. This it usually does by sharing, as in the hydrogen molecule H:H, or in a hydrocarbon. It can also, however, in

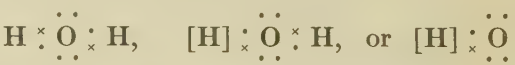
combination with highly electropositive metals, form a negative ion $[\cdot H\times]^-$; this behaviour was predicted by Lewis in 1916, and subsequently verified experimentally in the cases of lithium and calcium hydrides Li[H] and $Ca[H]_2$.

The elements from lithium (3) to fluorine (9) might either lose electrons so as to revert to the helium structure, or gain them so as to attain that of neon. As we should expect, the earlier elements tend to lose, and the later to gain electrons. Thus we have the simple ions Li^+ and Be^{++} with two electrons each, and O^{--} and F^- with ten. The formulae of their compounds are easily written (square brackets [ ] always enclose an ion).

The intermediate elements boron, carbon, and nitrogen do not form simple ions at all, but only covalent compounds, and as this necessarily involves an increase in the number of electrons, they never revert to the helium structure, but always progress towards that of neon: they strive to complete their octets. For this purpose carbon (boron will be dealt with later) needs four and nitrogen three more electrons. In consequence carbon combines with four and nitrogen with three hydrogen atoms, giving



in both of which the octets are complete. When we come to hydrogen and oxygen, there is a difficulty: water may equally well, so far as formulae go, be written



(in the ordinary symbols H–O–H, [H]O–H, or [H]O[H]), according as we regard the molecule as ionized (electrovalent) or not (covalent). The question can only be decided by considering the properties of water, which will be done later: but it is probable that (apart from polymers) water is a mixture consisting mainly of non-ionized but to a small extent of ionized molecules.

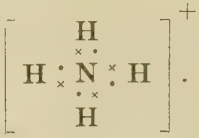
Most of the simpler organic compounds, in which the linkages are nearly always covalent, can be formulated quite easily on these principles. In such molecules as CH_3OH, H_2CO, $CH_3{\cdot}CO{\cdot}OC_2H_5$,

$CH_3{\cdot}NH_2$ it is only necessary to substitute two dots for every line in the full structural formulae : a single bond corresponds to two and a double bond to four shared electrons. It is scarcely necessary to say that such complete electronic formulae need not be adopted for ordinary use. Just as the student only writes the usual structural formulae in full until he understands them, and substitutes contractions like C_2H_5 or CO_2H as soon as he realizes what these contractions mean, so he need only use the electronic formulae until he is familiar with them ; he can revert to the simpler structural symbols as soon as he is able to transform them into their electronic equivalents when required, or when any difficulty arises. Almost the only one of the commoner organic groups whose conventional formula is modified by these new ideas is the nitro-group. On the classical theory this could be written in either of two ways : (1) $R{-}N\langle^{O}_{O}$ or (2) $R{-}N\langle^{O}_{O}$. The conception of the co-ordinate link introduces a new possibility, (3) $R{-}N\langle^{O}_{O}$, the nitrogen completing its octet at the nitroso stage R–N=O or $R{:}\overset{\times}{\underset{\times}{N}}{:}\overset{\times}{\underset{\times}{O}}{:}$, and in the formation of the nitro-compound sharing its remaining ' lone pair ' of electrons with a second oxygen atom. There is strong evidence that this third structure is correct. Nitrogen can be shown to be incapable of forming more than four covalent links, so that formula (1) is excluded : (2) is improbable owing to the great strain involved in a 3-ring (recent work has shown that 3-rings containing a nitrogen atom are much less frequent in organic chemistry than was previously supposed) : and finally the nitro-compounds show all the properties characteristic of molecules with co-ordinate links [1] (see Chapter VII).

The relations between tri- and quinquevalent nitrogen are easily explained in the light of the electronic theory. Nitrogen has five valency electrons, and so can complete its octet by taking up three hydrogen atoms. This octet is made up of six shared electrons and two unshared (a lone pair). If a fourth (neutral) hydrogen atom were taken up, this would introduce another electron, and the valency group would consist of nine, as it does in sodium (2) (8) (1). Hence (neutral) NH_4 behaves like a univalent metal : the valency group is unstable : it loses

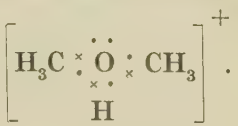
[1] This structure has recently been confirmed by Sugden's measurements of the parachor (see p. 127).

one electron readily if there is anything present that can receive it, and forms the stable ammonium ion



The core of the atom does not alter, and in that sense there is no real change of valency. This explains why it is found that one of the five valencies of quinquevalent nitrogen must always be an electrovalency : the formation of an electrovalency—the expulsion of an electron—is the condition of the nitrogen becoming 4-covalent. A nitrogen atom which has lost one of its electrons has four left, and so behaves like carbon. The resemblance extends to the positions of the four attached groups in space. In carbon they are as we know arranged at the points of a tetrahedron, giving optical activity when they are all different ; so also with nitrogen the four covalently attached groups of the ammonium ion have been proved to be at the points of a tetrahedron (Mills and Warren, 1925), and the optical activity is determined by them alone : the fifth group, the anion, is not attached to the ammonium ion in any fixed position, but merely attracted to it as a whole.

This principle, that an atom which has lost an electron resembles the preceding element, is (like the radioactive and the spectroscopic displacement laws) [1] a direct result of the theory of atomic number, and is of very wide application. Oxygen, having six valency electrons, can take up two hydrogen atoms or two methyl groups, and so complete its octet, which then consists of four shared and four unshared electrons : it is a divalent element. But if it loses an electron (and so acquires a positive charge) it becomes, like neutral nitrogen, a trivalent element ; for it then has five electrons, and has room for three more. Thus the oxygen in methyl ether $H_3C : \ddot{O} : CH_3$ is saturated in the same sense as the nitrogen in ammonia. But if it expels an electron it can take up a hydrogen atom, becoming



[1] pp. 7 and 37.

This of course can only be isolated in electro-combination with an anion such as $[Cl]^-$, and thus we have an explanation of the existence of the compound methyl ether hydrochloride $(CH_3)O{\cdot}HCl$, and of the oxonium compounds generally. The same change occurs with the halogens, though less easily and not with the lighter members, but certainly with iodine. The iodine in phenyl iodide $C_6H_5 : \underset{\cdot\cdot}{\overset{\cdot\cdot}{I}} :$ is saturated, having made its seven electrons up to eight. By losing an electron it acquires a positive charge and at the same time becomes divalent like neutral oxygen; it can thus form the ion $[C_6H_5 : \underset{\cdot\cdot}{\overset{\cdot\cdot}{I}} : C_6H_5]^+$ in the well-known iodonium salts, such as $[(C_6H_5)_2I]I$.

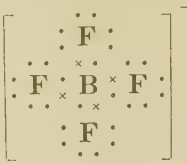
The elements of the fifth, sixth, and seventh groups—nitrogen, oxygen, and fluorine in the first period—are thus limited in their valency by the number of electrons for which they have room. Nitrogen can only take up three, oxygen two, and fluorine one, in order to complete the octet; and as every univalent atom or group brings an electron with it, their valencies in the neutral state are limited (apart from co-ordination) to three, two, and one, respectively. By expelling an electron and becoming cations they increase their valency by one.

With the elements preceding carbon (so far as they form co-valencies) there is the opposite difficulty. Boron, for example, has three valency electrons. It has room for five more; but it cannot take up five univalent groups, because it has not got five electrons to offer for the five links, but only three. Hence it can only take up three univalent groups, as in the fluoride BF_3 or the methide $B(CH_3)_3$ (the structure of B_2H_6 will be discussed later: it is almost certainly one of the rare instances of hydrogen attached by a single shared electron). In BF_3 the boron has lent one electron to each halogen atom, and borrowed one from each:

$$\begin{array}{ccccc} & & \cdot\cdot & & \\ & & F & & \\ & & \cdot\cdot & & \\ \cdot\cdot & & \cdot\cdot & & \cdot\cdot \\ F & \times & B & \times & F \\ \cdot\cdot & & & & \cdot\cdot \end{array}$$

so that the fluorines have completed their octets, while the boron has to be satisfied with six shared electrons, two for each link. This is an unstable condition, and atoms with incomplete octets are always ready to complete them. Now if the boron took up another electron, it would be able to combine with a fourth group: it would have four valency electrons like carbon, and

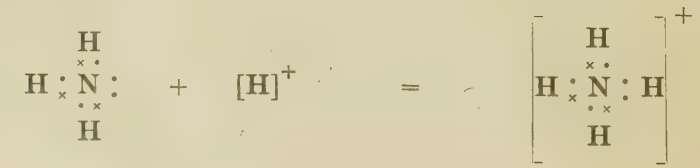
would like carbon be quadrivalent, but it would have a negative charge. It does this : it takes up an electron and a fourth fluorine atom, giving the stable anion $[BF_4]^-$, corresponding to $[NH_4]^+$, in which the octets of all the atoms are complete.



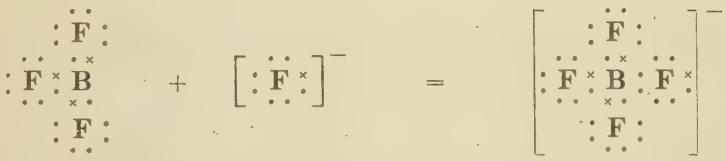
In this way we get a neutral and stable salt $K[BF_4]$, commonly described as a double salt, although no one would call the component BF_3 a salt.

A similar explanation applies to a more familiar series of ' double salts ', the silicofluorides. Sulphur, as we have seen, forms a very stable compound SF_6, in which it must have a valency group of twelve, lending one of its six electrons to each fluorine atom. Silicon has only four valency electrons, and so forms SiF_4. But if the silicon can gain two more electrons, giving it six like sulphur, it can combine with six fluorine atoms to form SiF_6, which of course has two negative charges. Thus in presence of a fluoride silicon tetrafluoride forms the stable anion $[SiF_6]^{--}$ of the silicofluorides $M_2[SiF_6]$. Aluminium, with three electrons to start with, can do the same thing if it gains three more : and so we get cryolite $Na_3[AlF_6]$.

This process, in which there is a change of valency accompanied by a gain or loss of electrons, deserves a rather more careful consideration. The most familiar example, the conversion of ammonia into the ammonium ion, has been described as consisting in the taking up by the ammonia of a neutral hydrogen atom, followed (or accompanied) by the expulsion of an electron. This is quite correct, but the same process may be described with equal truth in another way. The actual condition of the change is, as we all know, that the ammonia should come in contact with an acid, that is, with hydrogen ion. Presumably therefore the reaction should be written as taking place between an ammonia molecule and a hydrogen ion :



In that case we ought to say that the nitrogen of the ammonia shares its ' lone pair ' with the hydrogen ion, or that this hydrogen is attached to the nitrogen by a co-ordinate link. This is not only as true an account of the structure of the ammonium ion as that previously given, but it is really the same account in different language. On either view it is agreed that in the ammonium ion every hydrogen atom shares two electrons with the nitrogen : that in this way every hydrogen atom acquires the two electrons necessary to its stability, and the nitrogen atom its octet : and finally that the whole molecule has one positive charge ; which is explained on the first view by saying that since there are only eight valency electrons left in the octet, while one neutral nitrogen atom and four neutral hydrogen atoms originally had nine between them, one electron has been expelled ; and on the second view by the fact that a molecule made up of a neutral ammonia and a positive hydrogen ion must have a positive charge. It is not to be supposed that there is any difference between the linkage of the ' co-ordinated ' hydrogen to the nitrogen and those of the other three hydrogen atoms : each link consists of two shared electrons. In precisely the same way the formation of $[BF_4]^-$ or of $[SiF_6]^{--}$ may be described as due to the co-ordination of one fluorine ion to the boron, or two to the silicon :



Some confusion may arise from the statement that the co-ordinate link in such molecules does not differ from an ordinary covalency, when we have already adopted a special symbol to distinguish co-ordinate from normal covalencies : but the contradiction is only apparent. The co-ordinate link when it is established has the same mechanism as an ordinary covalency: the difference is in the way it is established. A normal covalency A—B between two atoms increases the number of electrons in each by one : a co-ordinate valency A→B increases the valency group of one atom (B) by two, while it leaves that of the other (A) unchanged. The symbol N—H means that each atom shares an electron previously belonging to the other. If we wish to express the fact that the fourth hydrogen atom in ammonium is a

co-ordinated hydrogen ion we should not write it N→H, since this would mean that the nitrogen shared its lone pair with a hydrogen *atom* (that is of course a neutral atom), which therefore would have three electrons—one which it had to start with, and two gained from the nitrogen. If it is to be treated as a co-ordination compound, the components are not ammonia and a hydrogen atom, but ammonia and a hydrogen ion, and the group would therefore have to be written $N{\rightarrow}[H]^{+}$, which indicates that the nitrogen has shared its lone pair with a hydrogen ion, and that this hydrogen now has two electrons—none to start with, and two gained from the nitrogen. But there is no point in using this complicated symbol when the outcome of the whole change is to link the fourth hydrogen to the nitrogen in the same way as the other three ; for they also are each joined by two shared electrons, and though we may say that here one of the two comes from the nitrogen and the other from the hydrogen, one electron does not in itself differ from another, and the only use in distinguishing their origin is to enable us to count them up correctly. In the same way $[BF_4]^{-}$ might be written

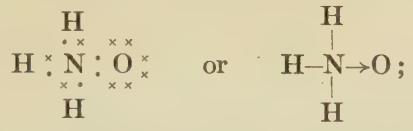
$$\begin{array}{l} \quad F \\ \quad | \\ F{-}B{\leftarrow}[F]^{-} \\ \quad | \\ \quad F \end{array}$$

, but this for the same reason is an unnecessary elaboration. Such formulae would indeed have a meaning if we wished to imply that the electric charge which the ion as a whole must possess resided in one particular atom. But there is no reason to think that it does so. The charge will be divided among the atoms of the ion in proportions depending on the time spent by the shared electrons in different parts of their orbits, about which we know little or nothing, except that the distribution will be uniquely determined by the number and nature of the atoms, and that the share of each of the hydrogen (or fluorine) atoms will be the same.

I have perhaps discussed this question at unnecessary length, but I have found that it is one which is not unfrequently misunderstood.

In these particular instances of $[NH_4]^{+}$, $[BF_4]^{-}$, and $[SiF_6]^{--}$, if they are regarded as co-ordination compounds, one of the components is an ion, and so the products are ions also. This however need not be so : two neutral components may form a co-ordinate link if one of them can supply a ' lone pair ' and the other can take it up. That an oxygen atom can act in this

way was recognized, as we have seen, by Lewis. Ammonia might form such a compound with oxygen



and though this compound is not known (unless it be as a tautomeric form of hydroxylamine), the corresponding oxides of the tertiary amines, such as trimethylamine oxide $(CH_3)_3NO$, are well established. They are commonly written with a double link between the nitrogen and the oxygen, but since we know that nitrogen cannot form more than four covalent links, they should obviously be formulated $R_3N{\rightarrow}O$. It is interesting that methyl-ethyl-aniline oxide, in which all the three hydrocarbon radicals are different, has been shown to be optically active.

With a link of this kind it is evident that the oxygen, which began as a neutral atom with a nuclear charge of + 8, balanced by two K (1-quantum) electrons and six valency electrons, has now acquired in addition a share in two more electrons, borrowed from the nitrogen. This must give it something of a negative charge, the nitrogen having a corresponding positive charge; and if we assumed that the two electrons are shared equally between the two atoms, we should conclude that the oxygen has one unit of negative and the nitrogen one unit of positive charge. For this reason Lowry writes the link $\overset{+}{A}{-}\overset{-}{B}$, as in $R_3\overset{+}{N}{-}\overset{-}{O}$, and calls it a semi-polar link: it is regarded as made up of one polar and one non-polar link (one electrovalency and one covalency). We know so little, however, about the mechanism of the sharing of electrons, or about the distribution of the charge among the atoms concerned, that it is perhaps safer to make no assumptions in the matter. We must recognize that the nitrogen in an amine oxide is essentially in the same state as in an ammonium ion, having eight shared electrons forming four covalent links; but it is better to adopt a symbol which does not prejudge the question of the distribution of the electrical charge, so long as it is realized that some degree of electrical polarity, in the sense discussed above, is produced by co-ordination.

Boron affords another example of a link of this kind. The boron atom in boron trimethide has, as we have seen, only six (shared) valency electrons. It can therefore take up two more, and so combines with ammonia to form $(CH_3)_3B{\leftarrow}NH_3$, a stable

compound melting at 56° and boiling at 110°. The occurrence of links of this type in the oxy-acids H_3PO_4, H_2SO_4, and $HClO_4$ has already been discussed.

In connexion with co-ordination the position of hydrogen is peculiar. In most of its compounds its stable valency group is two, as we should expect since this is the number in helium ; it attains this usually by forming a single covalency, but rarely, as we have seen, by direct transference of an electron, giving the negative ion $[H]^-$. But there is strong evidence that hydrogen can form a larger valency group of four electrons. This must of course be produced by co-ordination, the two extra electrons being borrowed from another atom. One of the strongest grounds for believing this is derived from the behaviour of hydrofluoric acid. While the other halogen acids have the simple formula HX, as we should expect, hydrofluoric is undoubtedly polymerized, and even in the vapour state contains H_2F_2 molecules, and higher polymers as well. The occurrence of a series of stable salts like KHF_2 indicates the same thing, and further shows that the polymer forms an anion $[HF_2]^-$. This must be formed by the combination of a molecule H–F with a fluorine ion : the ion must share one of its lone pairs with either the fluorine or the hydrogen of the H–F. It cannot be with the fluorine, since no other fluorides behave in this way, and we have reason to know that fluorine cannot have a larger valency group than eight. Hence the link must be formed with the hydrogen, which must take up, in addition to the pair of electrons which it already has, another pair from the fluorine ion, giving $:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}}:H:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}}:$. The formula of the acid is thus H[F→H–F]. This explains the polymerization, which indeed can proceed beyond double molecules, since we might have H[F→H–F→H–F] and so on : it also explains why the other halogen hydrides do not polymerize in the same way : for it is found that elements always tend to show their highest covalency in combination with fluorine.

Another argument is derived from the behaviour of water. This polymerizes, as we all know, and especially forms at low temperatures a triple polymer, the large molecular volume of which (the cause of the expansion of water below 4° and on freezing) indicates that it is a covalent compound, a view supported by the examination of its crystal structure. Now there is no way of formulating a polymer of H_2O with non-polar links

except by supposing that the oxygen of one molecule forms a co-ordinate link with the hydrogen of another, by which means of course any number of water molecules can be linked together :

$$\begin{array}{c} \quad\quad\quad\

V

VALENCY AND THE PERIODIC TABLE

IT may be useful at this point to consider briefly what light the ideas of valency so far advanced throw on the connexion between the chemical relationships of the periodic table and the theory of atomic structure. The form of the table already given (p. 39), which is best adapted to illustrate the Bohr theory of development, is less suitable for our present purpose. A more convenient classification of the elements into groups is secured by using a slightly modified form of Mendeléeff's table, with its eight (now nine) groups and their subgroups, which also has the advantage of familiarity. The only important departures from Mendeléeff's scheme are the introduction of the inert gas group (Group O), and the inclusion of the whole of the rare earth metals (La 57 — Lu 71) in Group III A. Every group except the first and last then has the same general form. Suppose we are considering the Nth group. In each of the two short periods (the ' period ' is taken to include, as in the Bohr scheme, all the elements between one inert gas and the next) it has one representative, the atom containing N more electrons than helium or neon : the first of these is commonly called the typical and the second the subtypical element, but we may conveniently use the word typical to cover both. In the three following periods (the two long periods and the rare earth period) each group has two representatives, the first of which is said to belong to the A and the second to the B subgroup.[1] Of these two the first (A) is characterized by having, like the typical elements, N more electrons than the inert gas at the head of the period (with a suitable modification in the rare earth period) ; the second (B) comes 8 — N places in front of the next inert gas. The whole of the chemical properties of the groups are determined by these structural relations.

The most fundamental distinction has already been indicated. Owing to the exceptional stability of the inert gas structures, the neighbouring elements will always tend to assume them : hence

[1] It is unfortunate that the words ' group ' and ' subgroup ' are used in two different senses : of groups of electrons in an atom, and of groups of elements in the periodic table. Usually the context makes the meaning clear ; wherever confusion seemed possible I have specified the sense in which the words are used.

Group.	I. A.	I. B.	II. A.	II. B.	III. A.	III. B.	IV. A.	IV. B.	V. A.	V. B.	VI. A.	VI. B.	VII. A.	VII. B.	VIII.	O.
Period 1.	H 1												H 1			He 2
2.	Li 3		Be 4		B 5		C 6		N 7		O 8		F 9			Ne 10
3.	Na 11		Mg 12		Al 13		Si 14		P 15		S 16		Cl 17			A 18
4.	K 19	Cu 29	Ca 20	Zn 30	Sc 21	Ga 31	Ti 22	Ge 32	V 23	As 33	Cr 24	Se 34	Mn 25	Br 35	Fe 26 Co 27 Ni 28	Kr 36
5.	Rb 37	Ag 47	Sr 38	Cd 48	Y 39	In 49	Zr 40	Sn 50	Nb 41	Sb 51	Mo 42	Te 52	Ma 43	I 53	Ru 44 Rh 45 Pd 46	X 54
6.	Cs 55		Ba 56		La 57 Ce 58 Pr 59 Nd 60 Il 61 Sm 62 Eu 63 Gd 64 Tb 65 Ds 66 Ho 67 Er 68 Tm 69 Yb 70 Lu 71		(Ce 58) (Pr 59) Hf 72		Ta 73		W 74		Re 75		Os 76 Ir 77 Pt 78	
		Au 79		Hg 80		Tl 81		Pb 82		Bi 83		Po 84		— 85		Em 86
7.	— 87		Ra 88		Ac 89		Th 90		Pa 91		U 92					

the elements at the beginning of a period will so to speak look back, and those at the end will look forward : the former will tend to lose and the latter to gain electrons, and the number which they lose or gain will be the difference between their own atomic numbers and that of the neighbouring inert gas. This is the reason why the earlier groups are metallic or electropositive in character, giving positive ions, while the later groups are electronegative, and give anions, or obtain the necessary increase of electrons by means of covalent links : and also why there is the simple relation between the valency of an element and its group-number which Mendeléeff first pointed out.

The properties of the elements are largely dependent on whether they can form simple ions or not, and whether these ions are positive or negative : the ' metallic character ' is essentially the power of forming positive ions. The conditions which determine ionization are primarily two. Firstly, the ion is more difficult to form the higher its valency : the removal or addition of each successive electron needs more work, owing to the resistance offered by the charge which the atom has already acquired. Secondly, the number of electrons which the ion still possesses must be capable of a stable arrangement. The most stable arrangements are of course those of the inert gases, and hence ions are most readily formed by elements only one or two places removed from an inert gas : indeed negative ions are only formed by such elements. But there are two other forms of electronic grouping which are stable enough to exist in cations. All the inert gases have an outer group of eight electrons ; but as we have seen, a structure in which this outer group is removed, and there is left an outer group of eighteen electrons, can have a very considerable degree of stability. Now in any group the ' compactness ', that is to say the tendency of the electrons to remain in that group instead of passing out into the next group of higher quantum number, increases with an increase of the electric field in which the electrons are moving—that is, of the nuclear charge. We have already seen two examples of this. The nineteenth electron, which in K and Ca^+ (nuclear charges 19 and 20) occupies a 4_1 orbit, in Sc^{++} (nuclear charge 21) is recalled to a 3-quantum orbit. In the same way the 18 group is only maintained as such if the nuclear charge is sufficiently large. Nickel 28 might form the groups (2) (8) (18), but we know that certainly one and probably two of the eighteen electrons go into the fourth quantum group, giving (2) (8) (16) (2).

In copper the nuclear charge of 29 is sufficient to maintain the 18 group, the structure being (2) (8) (18) (1), but it is only just sufficient ; chemical forces can easily remove one of the eighteen electrons, giving the cupric ion (2) (8) (17). In zinc 30 and in all higher elements the field is strong enough to maintain the 18 group against chemical attack. Hence in all the seven elements preceding an inert gas, or in all but the first of them, the group of eighteen electrons is of sufficient stability to persist, and so these elements show on the whole the same properties of ionization and valency as the elements of the two short periods. But these are the elements of the B subgroups, and this is what justifies us in classing them in the same groups with the typical elements.

The third type of core which is stable enough to exist in ions is that in which the outer group is an imperfect one containing between eight and eighteen electrons : this occurs in the transition elements in the wider sense, those which are enclosed in frames in the Bohr table (p. 39). These elements all form cations, the valency of which (except in the third group) is always less than the group number. The stability of the core is sufficient, but is small enough to be open to chemical attack, so that one or two electrons can be removed from it. Hence these are elements of variable valency. Iron, for example, gives two kinds of ions, the structures being :

Fe 26	=	(2) (8) (14) (2)
Fe^{++} 24	=	(2) (8) (14)
Fe^{+++} 23	=	(2) (8) (13)

These elements, it should be observed, form the A subgroups of the later periodic groups and the transitional triads of Mendeléeff.

These principles enable us to understand the distribution in the periodic table of the elements which form simple [1] ions. Cations are known with valencies up to four (for example, the stannic ion Sn^{++++}), but no anions of a higher valency than two. The reason for this difference is obvious : whereas an increase in the positive charge on an atom binds the remaining electrons more firmly, an increase in the negative charge weakens their attachment. Even in a univalent anion, since there is one

[1] The question how far ions in solution are covalent (co-ordinated) compounds of the simple ions with the solvent is one of great complexity, which will be considered later. For the present we may disregard it, and treat, say, the aluminium ion as a simple ion Al^{+++}, whether in solution it forms a co-ordinated compound with the solvent or not.

more electron than is equivalent to the nuclear charge, if this is removed to a distance the rest of the ion being neutral has no force to call it back. Accordingly we find that no simple anions are formed except those which have the same number of electrons as an inert gas (hydrogen, the halogens, and oxygen, sulphur, selenium, and tellurium). Such anions as Mn^- = (2) (8) (8) (8) or Co^- = (2) (8) (18) cannot exist because these electronic structures are unstable, the first always unless all the last eight electrons are shared, the second unless the nuclear charge exceeds the number of electrons in the structure.

Cations are more stable, and, for reasons which will be given in a later chapter (p. 104), their stability increases in any given group with the atomic number. Thus in the first short period only the first two members (Li, Be) form cations : in the second, the first three (Na, Mg, Al), but not silicon. A quadrivalent ion does not appear until much later, probably not before tin. No simple ions of a higher valency than four are known. In addition to these ions, all of which have the group valency, there are the ions of the transition elements in the wider sense, with valencies of two or three irrespective of their periodic group, which extend across the table to the end of the triads in Group VIII.

It must be understood that the powers of ionization and of covalency-formation are not mutually exclusive. All elements other than the inert gases, even the alkali metals, can form covalent compounds under suitable conditions. In particular the last element in its period which is able to ionize positively (for example, beryllium or aluminium) is always peculiarly prone to form covalent links. It is also found that among the earlier groups the members of the B subgroups are more ready to form covalent compounds than those of the A : thus in the second group the halides of calcium, strontium, and barium are obviously more salt-like in character (less volatile and less soluble in organic solvents) than those of zinc, cadmium, and mercury. This is due to the fact already mentioned that the valency electrons of the B elements are moving in a stronger electric field (owing to the smaller stability and screening effect of the electronic group of eighteen) than those of the A elements, as is shown by the much smaller atomic volume of the former.[1]

Another fundamental characteristic of the periodic table is that in the earlier groups the typical elements resemble the A subgroup rather than the B, while in the later groups they

[1] For a further discussion of this see p. 104.

resemble the B rather than the A. Thus in Group I lithium and sodium obviously form a closely allied series with the other alkali metals, while their affinities with copper, silver, and gold are slight. In the second group (Be, Mg : Ca, Sr, Ba, Ra : Zn, Cd, Hg) the differences are less marked, but still in the same direction. In the third group (B, Al : Sc, Y, La, &c. : Ga, In, Tl) the typical elements are almost equally related to both subgroups : in the fourth carbon and silicon have more affinity with the B subgroup (Ge, Sn, Pb) than with titanium and zirconium ; and in the fifth, sixth, and seventh groups the resemblance of the typical elements to those of the B subgroup becomes increasingly marked, until in the last of these we have the halogens from fluorine to iodine forming an unusually well-defined series, while their resemblance to manganese is almost confined to the similarity of the perchlorates and permanganates, which one is inclined at first sight to regard as little more than accidental.

These peculiar relations are a necessary result of the atomic structures, as can be seen by considering the stability of the respective atomic cores—the groups of electrons other than the valency electrons. The typical elements contain completely stable and unalterable cores of an inert gas number (2 or 10). The elements of the A subgroups start (in Group I) with a similar core, but as the nuclear charge increases this becomes unstable, its outer electron group of eight beginning to expand. At first (for example, in scandium) these new electrons are easily removed and act as valency electrons, and the core is still for practical purposes that of the inert gas. But as they become more numerous in the later groups, they are increasingly difficult to remove ; the core expands, and a new set of properties begins to appear. This is why the A elements resemble the typical elements in the earlier groups but become less and less like them in the later.

With the B elements the reverse process takes place. These have the group-number of valency electrons next to an electronic group of eighteen (instead of eight). This group of eighteen is much less stable than a group of eight unless there is an excess of positive charge on the nucleus, or in other words, unless the element belongs to one of the higher periodic groups. Hence in the earlier groups the instability of the core in the B elements gives them properties different from those of the stable-cored typical elements : this is especially so in the first group, where the core can actually break down with the production of a higher

valency (Cu, Au), but in the following groups also (as in the compounds of univalent copper and gold) there are marked differences due to the stronger field in which (owing to the smaller screening effect of the 18 group) the valency electrons are moving. As we reach the later periodic groups and the nuclear charge increases, the group of eighteen electrons is itself moving in a stronger field and is therefore more firmly held : its stability increases, and the resemblance of the elements to the typical increases likewise.

The atomic structures also explain the peculiar nature of the increasing divergence in properties which occurs in the later groups between the typical elements and the members of the corresponding A subgroups. As we go along the series—for example, Sc, Ti, V, Cr, Mn—the elements, instead of becoming increasingly electronegative, retain their metallic character in the elementary state and in many of their compounds, in which they show valencies unrelated to those of the groups to which they belong ; but they also form a second set of compounds of an acidic kind, whose properties are consistent with their places in the table, and in these compounds they show the group valencies. The reason can best be made clear by taking a particular instance, such as that of sulphur and chromium in Group VI. Sulphur (2) (8) (6) can complete its octet, assuming the argon structure (2) (8) (8), either by ionization (S^{--}) or by forming two covalencies as in H_2S, where four of the electrons of the octet are shared [1] (2) (8) (4, $\underline{2}$, $\underline{2}$). No such change is possible for chromium, because the corresponding structure (2) (8) (8) (8) is unstable : the last group would break down, and some of its electrons would go into the third quantum group, as happens in Fe 26 = (2) (8) (14) (2). Again, by forming a co-ordinate link sulphur can become trivalent, as in diphenyl sulphoxide $(C_6H_5)_2S\rightarrow O$, in which it has the structure (2) (8) (2, $\underline{3}$, $\underline{3}$). This also is impossible for chromium, because the two unshared electrons of the last group would pass into the preceding group, leaving an incomplete octet. By means of a second co-ordinate link the sulphur, as we have seen, can become quadrivalent, as in sulphuric acid $\begin{matrix} H{-}O \\ H{-}O \end{matrix}\!\!>\!S\!<\!\!\begin{matrix} O \\ O \end{matrix}$ or diphenyl sulphone $\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!S\!<\!\!\begin{matrix} O \\ O \end{matrix}$.

[1] The electrons of the octet are included in a bracket, the shared electrons being underlined. Thus (2, $\underline{3}$, $\underline{3}$) means that two of the eight valency electrons are unshared, and the rest (three pairs) are shared, forming three covalencies. See p. 164.

It now has the structure (2) (8) ($\underline{4}$, $\underline{4}$). Here at last we have a structure which is possible for chromium. In chromic acid $\begin{matrix}H{-}O\\H{-}O\end{matrix}\!\!>\!Cr\!<\!\begin{matrix}O\\O\end{matrix}$ it has the corresponding structure (2) (8) (8) ($\underline{4}$, $\underline{4}$). The outer octet being wholly shared, there are no electrons free to revert to the preceding quantum group, and a stable atom results. Selenium (2) (8) (18) (6) will of course behave like sulphur. The resemblance between chromium and sulphur or selenium or generally between an A element of one of the later periodic groups and the corresponding typical element or B element, is only to be found in those compounds in which all the valency electrons of both are utilized—with a valency of six in Group VI and of seven in Group VII—because it is only then that the preceding electronic group of eight in the A element cannot attract any electrons out of the valency group and thereby destroy the stability of the structure. Thus it is not an accident, but a necessity of the case, that confines the analogy between chlorine and manganese to compounds of the type of the perchlorates and the permanganates, exactly as that of sulphur or selenium and chromium is confined to such compounds as the sulphates or selenates and the chromates. These are the compounds in which the element has the group valency. The structure of chlorine in perchloric acid $\begin{matrix}H{-}O\\O\end{matrix}\!\!>\!Cl\!<\!\begin{matrix}O\\O\end{matrix}$ is (2) (8) ($\underline{4}$, $\underline{4}$), as that of manganese in permanganic acid $\begin{matrix}H{-}O\\O\end{matrix}\!\!>\!Mn\!<\!\begin{matrix}O\\O\end{matrix}$ is (2) (8) (8) ($\underline{4}$, $\underline{4}$). The last group is wholly shared, and this leaves no electrons to disturb the stability by migrating to an inner quantum group.

So far we have considered the properties peculiar to the typical or to the B elements, and those which they share with the A elements. The properties peculiar to the A elements (considering as before only the later periodic groups) are in particular the metallic characteristics, that is, the power of forming positive ions. An element like sulphur could only form a simple positive ion if it could lose all its six valency electrons, which, as we have seen, is impossible for any element : anything short of this would leave it with a highly unstable group of a small number of electrons ; for example, S^{++} would be (2) (8) (4). The last four must remain in the third quantum group, because the second quantum group of eight is incapable of expansion, and such a group of four would be too unstable to exist.

No such difficulty arises with chromium. The four ' valency ' electrons remaining in Cr^{++} are all in the third quantum group —(2) (8) (12)—and a group of twelve in this position, with a nuclear charge of twenty-four, is quite sufficiently stable, although by chemical action a third electron is very readily removed, giving Cr^{+++} = (2) (8) (11).

The eighth periodic group stands by itself, and has no resemblance in structure to any of those preceding it. It contains the three transition triads Fe, Co, Ni : Ru, Rh, Pd : Os, Ir, Pt. These are the elements containing eight, nine, and ten more electrons than an inert gas, or in the third triad more than the quasi inert gas number (2) (8) (18) (32) (8). Strictly speaking this group should perhaps be broken up into three : Group VIII, Fe, Ru, Os : Group IX, Co, Rh, Ir : Group X, Ni, Pd, Pt, so that the group-number might still correspond to the excess of electrons over a stable number. But the importance of this excess in determining the properties of the elements is comparatively small. Except in a very few compounds such as RuO_4, OsO_4, and OsF_8 they none of them exhibit the inert gas core : this has practically always expanded under the influence of the high nuclear charge, and the characteristic valencies are lower than the group-number would suggest. The elements belong essentially to the A class, and appear perhaps more peculiar than they really are, because there are no typical elements with which to compare them.

Thus it is seen that the Bohr theory, in the light of what we have already learnt of the mechanism of valency, can explain some of the most fundamental chemical characteristics of the periodic table. There are many more which can only be explained after a more detailed examination has been made of the various types of linkage, and the conditions of their formation. This therefore is the next subject which we have to consider.

VI

ELECTROVALENCY AND COVALENCY

THE electronic structure which we assign to an atom in a molecule depends on whether we regard its attachments to other atoms as electrovalent or covalent, and no theory of the relation between structure and stability can be attempted until this question is settled. The distinction between the two kinds of covalency, normal and co-ordinate, is of less importance. The primary question is whether the attachment is due to the sharing of electrons, or to the electrostatic attraction of oppositely charged groups. In this chapter we shall consider the various criteria by which we can distinguish between these two forms of link, and also the conditions which determine the conversion of one form into the other. The peculiarities of the co-ordinate link, the conditions of its formation, and the properties to which it gives rise, will be discussed later.

While the existence of these two forms of valency is generally admitted, at any rate in extreme cases, there is less agreement on the question whether they are essentially distinct, or pass into one another by insensible gradations. The latter view is a natural deduction from the hypothesis of the static atom. In hydrochloric acid, for example, we may imagine a hydrogen ion gradually approaching a chlorine ion until ultimately the two are in contact : at the beginning of this process the attachment of the two is electrovalent, at the end it is covalent, and with a static atom there seems to be no reason for drawing an arbitrary line separating the two conditions. This is the view of G. N. Lewis, whose ideas were originally based on the cubic octet, although with the progress of physics he has come to accept the dynamic atom. But if we completely accept the implications of the Bohr atom, in which the electrons are moving in quantized orbits, it would seem to follow that a linkage must be either of one form or the other, and that the transition must involve a quantum change ; although in some cases this change may very well be brought about by a change of conditions, as for example of solvent, and there may even be substances which consist, in the liquid or gaseous state, of a mixture of molecules of the two forms in equilibrium.

This view, that electrovalency and covalency are essentially

distinct states of linkage, is strongly supported by various lines of argument which will be developed later, especially by the fact, emphasized by Werner, that the covalency (co-ordination number) of an element is a characteristic of it in a series of compounds in which the electrovalency varies within wide limits (even with a change of sign) according to the nature of the covalently linked groups.

The differences in properties between electrovalent and covalent compounds, which provide at once the justification for assuming the existence of two kinds of link, and the criteria for deciding to which class a given link belongs, may be grouped under two heads.

I. In an ionized compound, though the oppositely charged ions are strongly attracted to one another, there is no real bond between them. They are free to take up any relative positions which are convenient, and as a rule will adopt a close-packed form. As this will under any given conditions be uniquely determined (at any rate in the liquid or gaseous state), only one arrangement is possible, and isomerism is excluded. In covalent compounds on the other hand the linking orbits form part of the constitution of each of the atoms concerned. Their positions in space (relative to the other orbits) are thus fixed, and cannot be altered, beyond the limits of comparatively slight distortion, without a complete rupture of the orbit, that is, a quantum change. Hence covalencies, unlike electrovalencies, are directed forces, and it is quite possible to have the same groups arranged round the same atom in more ways than one : in other words, structural and steric isomerism are possible only among groups whose constituent atoms are held together by covalent links.

II. In a covalent compound the electrical forces are more or less completely satisfied within the molecule, and the external field of force is small, whereas in an ionized molecule the electrical disturbance is greater, and there is a strong field of force outside. By an appropriate ' head to tail ' arrangement the molecules of an ionized compound can satisfy the attractions of this external field more completely. Hence the work required to separate the molecules is greater when they are ionized than when they are not. (We shall see later that co-ordinated molecules occupy in some sense an intermediate position in this respect.)

All the methods used for distinguishing ionized from non-ionized molecules depend on the application of one or the other of these principles.

The most obvious, the direct observation of ionization in solution, results from (I). Since the attachment of the ions is electrostatic, if we can dissolve the substance (without decomposition) in a medium of high dielectric power such as water, the ions will separate from one another, and can be detected by their conductivity. Werner, in his work on co-ordination compounds, was careful to establish the presence of electrovalencies in this way. It is also possible, by measuring the conductivity at various dilutions, to determine not only whether the molecule is ionized at all, but also how many ions it yields. The differences in velocity between ions other than hydrogen and hydroxyl are small, and so the absolute value of the conductivity gives, especially by comparison with other similar salts, a fair indication of the number of ions into which the molecule divides. Further, Ostwald has shown that the change of molecular conductivity of a salt with dilution differs according as it gives two, three, or more ions, and is much the same for different members of any one of these classes, so that this magnitude also serves to show to which class a compound belongs.

The usual methods of molecular weight determination in solution, such as the cryoscopic, can also be employed to determine the degree of dissociation. Further, we can use any tests, physical or chemical, for the presence of the particular ions in question. Their concentration may be measured by means of the E. M. F. with a reversible electrode : this method is often used to determine the extent of the formation of the complex ion of a double salt, as in the complex cyanides, or the complex copper compounds of the hydroxy-acids.

Any available chemical tests may also be used. Thus chlorine may be tested with silver nitrate, which will precipitate silver chloride if the chlorine is ionized, but not otherwise. In this way it was shown that in the three forms (two green and one violet) of hydrated chromic chloride all of which have the composition $CrCl_3$, $6H_2O$, respectively one-third, two-thirds, and the whole of the chlorine is in the ionized state, giving the formulae

Green form (1)	Green form (2)
$[Cr(H_2O)_4Cl_2]Cl, 2H_2O$	$[Cr(H_2O)_5Cl]Cl_2, H_2O$

Violet form

$[Cr(H_2O)_6]Cl_3$

Conversely, the presence or absence of silver ions in a solution of a double salt of silver can be detected by the action of an

alkaline halide. For example, the soluble silver sodium thiosulphate $Na[S_2O_3Ag]$ gives a precipitate with sodium iodide, but not with sodium chloride. This shows that the silver is almost wholly in a covalent state, but that the complex ion is to a minute extent dissociated, with liberation of silver ions. We can even calculate roughly the concentration of these ions. The solubility products at the ordinary temperature are approximately : AgCl 10^{-10}, AgI 10^{-16}. Hence if the halide used is decinormal, the normality of the silver ions lies somewhere between 10^{-9} and 10^{-15}.

These direct tests for ionization can only be applied to a substance which is soluble without decomposition in an ionizing solvent (practically always water) : they obviously could not be used with silicon tetrachloride or phosphorus pentachloride. Even when the compound is more stable and is not obviously decomposed by water, a reaction may take place. Complex ions may dissociate to some extent into their simpler components : thus the fluosilicates will give reactions for fluorine ion. Similarly covalent chlorine may be replaced by hydroxyl or water (hydrolyzed) ; the second green form of chromic chloride slowly changes on standing in solution into the violet form, and all the chlorine can then be precipitated by silver. Such changes can usually however be detected when they occur, and so do not invalidate the ionization tests where these give definite results ; but they limit their application very seriously.

A conclusive proof of the presence of covalent links, but one which is even more limited in its application, is the existence of isomerism, and especially of stereoisomerism. If a molecule is optically active, although the groups attached to the central atom are not, we may assume that they are covalently attached. Any ionized groups, since they are not joined by directed forces to the central atom, must take up positions uniquely determined by the other atoms in the molecule : there cannot be two alternative positions possible for them. The same arguments apply to isomerism in general, provided that it can be shown to occur in the liquid or dissolved state ; the same individual molecules can sometimes take up several different crystalline arrangements. These tests are of course limited to particular kinds of compounds. But if we find, for example, that those six co-ordinated chromium compounds whose structure would admit of optical activity if the six groups were covalently linked, do actually exhibit this activity, we can infer not only that the links are

covalent in these compounds, but also that they are so in other inactive compounds of the same general type.

Where these criteria fail we have to rely on other and less precise tests. These are often quite sufficient when our object is to determine not whether a complex salt dissociates into two or into three ions, but whether a substance is a salt at all. We can then make use of any of those properties which distinguish a salt from a covalent compound.

The most obvious of these is the volatility. As we have seen, one characteristic of ionized molecules is that, as they have stronger external fields of force, they are more strongly attracted to one another than covalent molecules, and more work is required to separate them. The boiling-point of a substance is lower, the less the thermal agitation required to overcome the mutual attraction of the molecules. It is simply related to the work of separation (heat of evaporation), as is seen from Trouton's rule that the molecular heat of evaporation is approximately twenty-one times the boiling-point in degrees absolute. This rule does not hold for substances with very low boiling-points like helium and hydrogen, and only roughly for the 'permanent' gases; but for other substances it gives a fair approximation, except for highly associated liquids like water (25·9) and ethyl alcohol (26·9), where the molecular weight is uncertain. Generally speaking, we may take it that the heat of evaporation of a substance boiling at 0°C. is 6, at 100° is 8, at 500° is 16, and at 1000° is 27 kilogram-calories per gram-molecule approximately.

Hence a covalent compound will in general have a lower boiling-point than a salt. The most striking example of this is given by the hydrides of the elements. With the exception of a few hydrides of transition elements, such as palladium, copper, cerium, &c., whose chemical individuality is doubtful, the binary hydrides fall sharply into two classes.[1] All the nineteen known elements one, two, three, or four places before an inert gas, and also boron (but nothing else) form hydrides which are volatile and, so far as they have been examined, practically non-conducting, like methane: these are obviously covalent compounds. On the other hand the alkali metals and those of the alkaline earths form non-volatile hydrides, which are good conductors in the fused state, and on electrolysis liberate hydrogen at the anode, showing that they are salts containing the negative hydrogen ion.

[1] **Paneth, *Ber.* 1920, 53, 1710.**

The halides of the elements show a similar differentiation into volatile non-salts and non-volatile salts. The two classes differ not only in the absolute values of the boiling-points, but also in the effect on the boiling-points of the replacement of one halogen by another. A metal such as sodium forms halides which are typical salts : and these have very high boiling-points which fall slowly as the atomic weight of the halogen increases. The halides of non-metals such as carbon or silicon have comparatively low boiling-points, but these rise rapidly as the atomic weight of the halide increases. The following table gives some examples :

BOILING-POINTS IN °C. AT 760 MM. PRESSURE

NaF	NaCl	NaBr	NaI
1695°	1441°	1393°	1300°
SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
− 90°	+ 57°	153°	ca. 290°
AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
ca. 800°	183°	260°	350°
SnF_4	$SnCl_4$	$SnBr_4$	SnI_4
705°	114°	203°	300°

This sharp difference in properties indicates an equally sharp distinction in structure, and it is evident that the compounds of the first class (high boiling-points, falling from F to I) are salts, while those of the second are covalent. The opposite effect of a change of halogen in the two classes is what we should expect. The volatility of a normal substance is less the greater the molecular weight, and hence in the non-polar halides the boiling-points will rise as we go from the fluoride to the iodide. But in the salts the determining factor is the electrostatic attraction of the charged ions, and as the charges are the same this force must diminish as the atomic diameter of the halogen increases. The absolute boiling-points of the sodium salts are roughly in inverse ratio to the distances between the atomic centres in the crystals, as determined by the Braggs from X-ray measurements.

It will be observed that with elements of an imperfectly metallic character, like aluminium and tin, we do not find that the halides as a whole are intermediate in properties between the two classes, but that the fluorides clearly belong to the salt class, while the chlorides, bromides, and iodides have the normal behaviour of the covalent class, the boiling-points being fairly low, and rising rapidly with the rise in atomic weight of the halogen.

It is thus a general characteristic of ionized compounds to be non-volatile, and of covalent molecules to be volatile. With many compounds however the volatility cannot be observed directly, because they decompose below the temperature at which the vapour pressure becomes measurable. For such substances a qualitative estimate of the ionization or otherwise may often be arrived at through the solubility. This question cannot be fully discussed until we have dealt with the properties of associated liquids, which involves a more detailed examination of the co-ordinate link. But this much may be pointed out. The mutual attraction between the molecules of a solid salt, which diminishes its volatility, will also tend to lower its solubility. But a solvent of high dielectric capacity like water will diminish the forces between the ions by lowering their potential; and it can further promote solution by combining with the ions. This is why we find salts (like sodium chloride, B.Pt. 1441°) which are very soluble in water, although their vapour pressure at the ordinary temperature must be infinitesimal, and their melting points are very high. But a solvent of low dielectric constant and saturated character like a hydrocarbon (D.E.C. about 2, while that of water is 81) has but a very slight electrical and no chemical effect: it therefore cannot overcome the attraction of the ions, and salts, as we know, are in general insoluble in hydrocarbons. Hence if we find that a substance will dissolve fairly readily in such a solvent as benzene, we may assume that it is not ionized.

There is one caution which must be borne in mind, in considering both the volatility and the solubility. These properties are diminished by the presence of electrovalencies, but they are also diminished, for obvious reasons, by an increase in molecular weight, and therefore by polymerization or association. The effect of these changes in ordinary cases (where only a few molecules are so combined), though perceptible, is not great enough to be mistaken for that of ionization. For example, in the table of boiling-points on p. 88 it will be seen that those of the aluminium compounds are, apart from the fluoride, higher than those of the tin compounds, although the formula-weights of the latter are greater. This is due to the polymerization of the aluminium halides, of which the true formula at the B.Pt. is Al_2X_6. But the resulting elevation of the boiling-points is not comparable with that which ionization would produce.

On the other hand, there are certain substances of which the

whole crystal forms one great molecule, with all its atoms held together by covalent links. Of these ' giant molecules ' (Riesenmoleküle) the best-known examples are diamond and carborundum CSi. Such a molecule has, properly speaking, no vapour pressure or solubility : it can only melt or boil by actually dissociating, and owing to the firmness of the linkages this usually requires a very high temperature. These substances might easily be mistaken for ionized compounds : their non-polar character can only be ascertained by examination of the structure of the solid.

Ionization and Crystal Structure.

This brings us to the question how far the nature of the linkages can be established by the determination of the crystal structure by X-ray analysis. This appears to be, and no doubt will become, a very fruitful field : but at present the results have to be treated cautiously. It is only in the simpler forms of crystal that they afford much help, and the interpretation of the data from this point of view is only beginning. With the simpler inorganic salts, such as sodium chloride, we have direct evidence of ionization in the solid from the phenomenon of residual rays (Reststrahlen) of Rubens. The atoms of a crystal have their natural frequencies of vibration, and if they are charged—if the crystal forms an ionic lattice—these vibrations will cause an abnormally high reflection of incident light of the same frequency, by a direct process of resonance (not a quantum exchange). The actual frequencies are far in the infra-red [1] (with sodium chloride about 50μ or 500,000 Å.U.), and the phenomenon can be detected by allowing a beam of infra-red rays from a heated body to suffer repeated reflection from the surface of the crystal, when the other wave-lengths are absorbed, and those corresponding to the characteristic frequencies survive. These results make it certain that the salts examined are ionized even in the crystalline state.

But the usual method of examining crystal structure is by means of X-rays, a method originated by Laue, and developed especially by W. H. and W. L. Bragg and by Debye. It consists essentially in using the crystal as a diffraction grating, with rays of known frequency, and so determining the distances between the reflecting centres of the crystal lattice itself. The rays must

[1] Rubens and v. Wartenberg, *Sitzb. K. preuss. Akad.* 1914, 169 ; cf. Fösterling, *Ann. d. Phys.* 1920, **61**, 577.

be of the same order of wave-length as the distances between the atoms of the crystal (a few Å.U.), and so X-rays must be used. It can be shown that the reflection is due to the electrons and not to the nuclei of the atoms. It was at one time supposed that the number of electrons in the atom could be determined in this way from the intensity of the reflections, and that the results obtained with lithium fluoride proved that the lithium atom had two and the fluorine ten electrons, indicating the transference of an electron by ionization. Later work has made it doubtful whether the results are accurate enough to justify this inference. There is no doubt however that the X-ray method gives us, even with salts of considerable complexity, an accurate picture of the disposition of the atoms in the crystal, from which valuable conclusions can be drawn as to the nature of the linkage between them.

In the simplest cases of the alkaline halides two types of structure occur, known as the rock salt and the caesium chloride lattices. In the first each sodium atom is surrounded symmetrically by six chlorine atoms, and each chlorine by six sodiums : the second is similar, except that the number is eight instead of six. These structures are exactly what we should expect if the atoms of the lattice are really ions, with no attachment to one another beyond their electrostatic attractions. They are close-packed systems, and there is no indication that a particular sodium atom is more closely linked to one chlorine than to any of the other five. In a crystal like calcium carbonate we find the same kind of relation between the calcium ion and the CO_3 ion, but a different one for the constituent atoms of the CO_3 group itself : here the three oxygen atoms have a relation to one another and to their own carbon different from that which they have to those of any other CO_3 groups ; and this may be taken as evidence that the calcium and the CO_3 are themselves ions, but that the atoms of the CO_3 group are covalently linked to one another. Similar results have been obtained with more complex compounds. In $NiCl_2, 6NH_3$ it has been shown that the six ammonias are arranged symmetrically (at the points of an octahedron) round the nickel : an identical arrangement of the six chlorine atoms round the platinum has been observed in ammonium platinichloride, and of the six water molecules round the zinc in zinc bromate hexahydrate. We may therefore assume in these salts complex ions whose atoms are covalently united, as indicated in the formulae $[Ni(NH_3)_6]Cl_2$, $(NH_4)_2[PtCl_6]$, and $[Zn(H_2O)_6](BrO_3)_2$.

When we find that a molecule has an elaborate and open structure, occupying a large volume, we may assume that the linkages are covalent, or the parts would be more closely packed. This is what happens with ice,[1] which has a very diffuse molecule, apparently of the formula H_6O_3.

This line of argument has recently been developed with great ingenuity by Grimm and Sommerfeld.[2] They have classified the crystal structures of all compounds hitherto examined of the general formula AB (1 : 1 compounds of two elements) in which an atom of A and one of B have eight valency electrons between them. They find that four types of lattice occur : the rock salt and caesium chloride types already mentioned, with each A surrounded by six or eight B and vice versa, and the diamond and wurtzite (ZnS) types, which both have four A atoms arranged round each B at the points of a tetrahedron. These two latter forms are not close packed, and the authors conclude that whereas the first two types (rock salt and caesium chloride) represent ionic lattices, the last two are covalent, and the crystals in these cases (e.g. carborundum CSi, AlN, and even BeO) are ' giant molecules ' in which all the atoms are joined by shared electrons. Where A and B belong to different periodic groups, we must suppose that the eight electrons are first divided equally between them, giving four to each atom, which are used to form four covalencies : so that in a sense we may say that the formulae should be written $Al^{-}N^{+}$ and $Be^{--}O^{++}$, although the atoms are not ions, but are covalently linked throughout the crystal. The results of this work will be considered in more detail later.

The Transition between Electrovalencies and Covalencies.

As we have seen, there is good evidence that some molecules, like those of sodium chloride, are always ionized, even in the solid, and that others, such as methane, are never ionized, but always held together by the sharing of electrons. But with many substances the evidence is that in some states they are ionized, and in others they are not. Examples of this are found among the halides of the polyvalent elements. Stannic chloride, for instance, is a volatile liquid miscible with benzene, and is a non-conductor of electricity. In the absence of hydroxylic solvents

[1] W. H. Bragg, *Proc. Phys. Soc.* 1922, 34, 98.
[2] *Z. f. Physik*, 1926, 36, 36.

it has all the characteristics of a covalent compound. But in water it is evidently ionized, and gives the reactions for stannic and chlorine ions. We cannot but conclude, in spite of its behaviour in water, that in the pure state and in non-ionizing solvents it is a covalent compound. It is quite possible to argue that strictly speaking $SnCl_4$ is always covalent, and that what is formed when it is dissolved in water is an ionized compound with the solvent, such as $[Sn(H_2O)_6]Cl_4$, which is certainly the composition of the solid which separates from the water. This however is of secondary importance; the main point is that a substance which when dissolved in water undoubtedly gives rise to ions, may in the absence of water be a non-polar compound. The trivalent chlorides of aluminium and iron behave in the same way: they are volatile (at least in comparison with an alkaline chloride), they dissolve in hydrocarbons, they are non-conductors, and generally in the absence of water they show the properties of covalent compounds. In water they give chlorine and aluminium or ferric ions, and the salts which separate contain in both cases six molecules of water of crystallization. Here again it is very probable that the combination with the water renders the ionization possible. A similar instance is that of the halogen hydrides. These with the exception of the polymerized hydrogen fluoride are gases of low boiling-point, do not conduct in the pure liquid state, and are soluble in hydrocarbons. If their behaviour in dissociating solvents were unknown, no one would doubt their covalent character. But in water they are of course practically completely dissociated into their ions.[1]

For these reasons it is clear that a molecule can pass from the ionized to the covalent state and vice versa, with a suitable change of conditions.

Weak Electrolytes.

A more difficult question is whether, when a substance is dissolved in water and partly dissociated into ions, the non-dissociated portion is wholly held together by electrovalent links, or whether it forms an equilibrium mixture of non-dissociated ionized molecules and covalent molecules, as represented by the equation $[R]A \rightleftharpoons R{-}A$, or is wholly in the latter (covalent) form.[2]

[1] Compare Biltz and Klemm, *Z. anorg. Chem.* 1926, **152**, 267.

[2] The terms 'dissociated' and 'ionized' are commonly used in the discussion of electrolysis as if they were synonymous; but now that we

With strong electrolytes this question does not necessarily arise. The recent theory of Debye explains satisfactorily the ' anomaly ' of strong electrolytes without needing to assume anything in the solution except the two kinds of ions at varying distances from one another, and finds the cause of the difference between the change of conductivity with dilution and the law of mass action essentially in the fact that the electrical forces between ions act over longer distances than the chemical forces between neutral reacting molecules. It is commonly said that this theory involves the complete dissociation of the strong electrolyte. It would perhaps be more correct to say that it involves its complete ionization (which is indeed already established for salts like the alkaline halides by the determination of the crystal structure and the observation of the ' Reststrahlen '[1]), and that it abolishes the distinction assumed by Arrhenius between a dissociated portion, in which the opposite ions were without action on one another, and an undissociated portion, in which they were in contact ; the truly undissociated (but still ionized) part now appears as a limiting case, in which the distance between the opposite ions is reduced to a minimum. The apparent fall in the ionization of a salt (whether this is measured by the conductivity or the osmotic properties) is adequately accounted for by the restraining influence of the ions on one another, due to their electrical charges.[2] This causes a strong electrolyte, which is completely ionized and practically completely dissociated, to have at moderate dilutions a molecular conductivity which (for a uni-univalent salt) is something like 80 per cent. of that at infinite dilution. It is difficult to imagine that the size of the ions, or the nature of the electrolyte (so long as it is completely ionized, and we are dealing solely with the electrical forces between the ions) can greatly affect this ratio ; indeed it has been shown that for normal salts it is almost wholly determined by the valency of the ions, being in decinormal solution for a salt M′X′ 84 per cent., for $M''X_2'$ 74 per cent., and for M″X″ 40 per cent.—in all cases within two or three

recognize two forms of linkage it is clear that an undissociated molecule may be either ionized (electrovalent) or covalent.

[1] p. 90.

[2] This does not exclude the possible presence of a minute concentration of non-ionized (covalent) solute, where there is independent evidence of its existence : as in certain strong acids like hydrochloric, which have a measurable vapour pressure in aqueous solution.

units, whatever the salt examined: and these values are in accordance with the Debye theory.

But when we come to weak electrolytes, we find that the apparent dissociation (however it is measured) is of a different order of magnitude. Moreover it is a remarkable fact that while some acids and bases are strong and others are weak electrolytes, salts are strong electrolytes, whether the acids and bases from which they are formed are strong or weak. Ammonium acetate has nearly the same apparent ionization as sodium chloride, although both ammonia and acetic acid are weak. To put it in figures, the molecular conductivities of sodium chloride, sodium hydroxide, hydrochloric acid, and ammonium acetate at moderate dilutions are all about 80 per cent. of the values at infinite dilution, while those of acetic acid and ammonia are only about 1 per cent.

This strongly suggests that an electrovalent link is always dissociated in water to about the same almost complete extent: that if only the ionized form is present we shall always find the apparent ionization in a normal solution to be some 80 per cent.: and that the low conductivity of weak electrolytes is due to two forms being present in the solution in equilibrium, an electrovalent and a covalent form, the first being dissociated to the same extent as a strong electrolyte, but being present only in small quantity. For example, in normal acetic acid, where the conductivity indicates a dissociation of 0·4 per cent. we might have 99·5 per cent. of the acid in the covalent form [$CH_3 \cdot CO \cdot OH$], and 0·5 per cent. in the electrovalent form [$CH_3 \cdot CO \cdot O$]H, with a molecular conductivity four-fifths of that at infinite dilution. The position of the equilibrium between these two forms will obviously depend not merely on the charges of the ions, but on their chemical nature. Now this feeble ionization is confined (with the exception of the salts of a few metals, such as cadmium and mercury, which will be considered later) to some inorganic and most organic acids, and many organic bases, including ammonium and phosphonium hydroxides. If our theory is sound, there must be some reason why substances of these kinds are peculiarly easily able to pass from the electrovalent to the covalent state, and some evidence from their physical and chemical properties that they do so.

Taking first the acids, we have to explain why they have a tendency to assume the covalent form which is lost when the acidic hydrogen is replaced by a metal. Now G. N. Lewis has

pointed out that hydrogen occupies a peculiar position in that the number of electrons which the hydrogen ion needs for stability is two, which is the precise number that it gains when it passes from the ionized to the covalent state :

$$H^+ + :X^- \longrightarrow H:X$$

But a metallic ion needs eight, and the condition of a metallic ion to which only two shared electrons have been added (as in sodium ethide) is excessively unstable. Hence the transformation into the covalent link will be far easier with hydrogen than with metals, and acids must have a power of changing into the covalent form which is in general denied to salts.

Again, it has been known for some time that the order of strength of acids is quite different in other solvents from what it is in water, and that the difference cannot be explained by the electrolytic theory alone ; for example, the strength of perchloric, hydrochloric, and nitric acids in water is about the same, all three being highly dissociated, while in ether (as measured by their chemical activity) it is roughly in the ratio 100 : 1 : 0. Hantzsch has recently [1] argued in great detail in favour of this view, that all acids have the power in varying degrees of passing (for example, with a change of concentration or solvent) from a polar to a non-polar form. He supports this by evidence drawn from a very wide range of phenomena, especially the change in absorption spectrum and in chemical properties as the solvent is varied. He finds that these properties on the whole go together ; the absorption spectrum of the acid is as a rule intermediate between that of its salts and that of its esters, and inclines towards the ester type under conditions where the chemical properties indicate a predominance of the covalent form. These conclusions are supported by the general behaviour of weakly acidic organic compounds such as carboxylic acids and especially alcohols and phenols, which under conditions that do not favour dissociation is that of covalent rather than that of undissociated electrovalent compounds. This is what we should expect if they exist in two quasi tautomeric forms, one electrovalent and the other not.

This view is strengthened by the behaviour of the ammonium bases. We all know that ammonium hydroxide is a weak base

[1] *Z. f. Elektrochem.* 1923, 29, 221. His arguments have been attacked by v. Halban (ibid. 434), who has certainly weakened the force of some of them. But even so the balance of evidence seems to be clearly on Hantzsch's side.

(of the same strength as acetic acid), and that the replacement of the hydrogens by methyl or ethyl groups increases its strength, but not very greatly until all four have been replaced, when we arrive at $[NAlk_4]OH$, which is almost as strong as caustic potash. This sudden increase of strength—from that of a weak to that of a strong electrolyte—on passing from a tertiary to a quaternary compound was formerly explained by the very natural supposition that the equilibrium

$$NR_3 + H_2O \rightleftharpoons NR_3HOH \quad (R = H \text{ or alkyl})$$

which must obtain in a solution of ammonia or an amine, lies very far on the side of the anhydrous amine ; so that in triethylamine, say, there is in solution a very small quantity of the highly dissociated NEt_3HOH and a large proportion of NEt_3, producing the effect of a rather weak electrolyte ; while in the quaternary compound NR_4OH, the dissociation to the tertiary amine being impossible, the full strength of the ammonium compound is exhibited. This view (which still survives in some quarters) was upset some time ago by Moore and Winmill,[1] who showed that it was possible, by measuring the conductivity of the base and also its partition between water and another solvent at several temperatures, to determine the amount of the free unhydrated amine in the solution, and hence the true dissociation constant of the ammonium hydroxide. The values which they obtained for this constant are given in the following table ; that for the quaternary hydroxide, which is added for comparison, is of course only rough, as the compound does not obey Ostwald's law.

True Dissociation Constants ($\times 10^4$) of Ammonium Bases at 18°.

	NH_4OH	NRH_3OH	NR_2H_2OH	NR_3HOH	NR_4OH
R = CH_3	0·294	4·87	14·21	0·72	ca 10,000
R = C_2H_5	0·294	6·73	10·59	7·87	ca 10,000

It is thus clear that the introduction of the fourth alkyl group makes an enormous difference in the strength of the base, which becomes of quite another order. Thus the current explanation, that primary, secondary, and tertiary amines are weak bases only because they can lose water, was disproved, and it became evident that R_3NHOH is really a weak electrolyte while R_4NOH is a strong electrolyte.

If we accept the view that a weak electrolyte exists in solution largely in a covalent form, ammonium bases like $[NR_3H]OH$

[1] *J. C. S.* 1907, **91**, 1373 ; 1912, **101**, 1635.

must be able to pass over into such a form ; but the change must involve a hydrogen attached to the nitrogen, since the base remains weak so long as one such hydrogen is present, but becomes strong (i.e. the covalent form vanishes) as soon as the last hydrogen is replaced. This can only mean that the hydroxyl forms a covalent (co-ordinate) link with this hydrogen

We know that hydrogen can sometimes assume a covalency of two ; and though there is not much evidence of its doing so in ordinary cases when it is attached to nitrogen, it is obvious that in this reaction the electrical charges will greatly promote the change. When all the hydrogens are replaced this change is no longer possible, since we have evidence that hydrogen atoms in an alkyl group have not this power.[1]

In this way the theory that a weak electrolyte consists of a covalent and an electrovalent form in equilibrium enables us to account for the peculiar behaviour of the nitrogen bases.

Orbits of Shared Electrons.

The question of the real meaning of the ' sharing ' of electrons has so far been left open. It is an obvious suggestion that as a ' lone ' electron encircles one nucleus, so a shared electron encircles two, though perhaps all that we are entitled to say at the moment is that its orbit is related to the two nuclei. The chemical evidence does however go far to show that the relation to both nuclei is the same in character : that such an orbit is not merely the orbit of the unshared electron somewhat distorted by the presence of the second nucleus, but that it actually forms part of the system of orbits of both atoms, and as far as we can see in the same way. We may therefore assume that while the shared electron is in the neighbourhood of each nucleus, its orbit is of the same general kind as those of the unshared electrons of that nucleus. This would explain why such an electron counts as one towards the stable electron number for each atom.

Now [2] on the Bohr theory the elliptical orbits (which most of the valency electrons occupy) consist essentially of two parts :

[1] This explanation of the behaviour of the amines was put forward by Latimer and Rodebush, *J. Amer. Chem. Soc.* 1920, **42**, 1419.

[2] Cf. R. H. Fowler, *Trans. Faraday Soc.* 1923, **19**, 459.

(1) inner loops, in which they come near the nucleus, and the attraction of the latter being great, move with a high velocity ; (2) outer loops, in which they are far from the nucleus and move much more slowly. For the maintenance of the stability of the atom the important part of the orbit is the inner loop, and the essential point is that the various electrons of a subgroup should pass through this loop in the right directions in space, and in due succession in time. In the outer loop their motion is less important, provided they return to the inner loop after the proper interval. Hence there seems to be no difficulty in supposing that the electron having gone through the inner loop round one nucleus might go over and perform the same service for the other : in which case it would count as an electron for each. We may also suppose that of the two electrons forming the covalent link one will be near one nucleus when the other is near the other.

This will also account for the fixed positions in space occupied by the attached atoms, since the planes of the linking orbits will be definitely related to one another. We can also see that if the structure of the molecules causes these atoms to be displaced from their natural positions, this will cause strain and instability in the molecule, as the Baeyer theory of strain demands. A further deduction from this idea relates to double links. Chemical evidence shows that two singly linked atoms can rotate (with their attached atoms or groups of atoms) round the line joining their centres so as to take up the most stable configuration, so that a compound of such a formula as $H_2XC–CXH_2$ can only occur in one form : but that with two doubly linked atoms, as in $HXC=CXH$, this no longer possible. It is evident that if in such a double link we have four electrons shared between the two atoms, their orbits must start out from one atom in planes inclined at the normal angle. This means that the relation between two doubly linked atoms is of the same kind as that between two atoms forming part of a ring ; and free rotation is as impossible in one case as in the other.

In general terms, then, the conception of binuclear orbits seems to fulfil the necessary requirements. But when we try to enter into details we meet with great difficulties. The physicists are only beginning to learn how to deal with the dynamics of such systems,[1] and no satisfactory theory has yet been given even of the simplest of them, the hydrogen molecule. In these

[1] Cf. Niessen, *Physikal. Z.* 1926, 27, 299.

circumstances the fewer assumptions the chemist makes, the better; and for our purposes little more is required than to suppose that a shared electron counts as part of the constitution of both atoms, and that its orbit is in general similar to those of the unshared electrons, but with some differences; of the effect of these differences on the stability we may hope to learn something from an examination of the chemical evidence, but for a dynamical explanation we must wait until the physical and mathematical difficulties have been overcome. There are, however, certain considerations which deserve attention.

I. The second quantum number k of the Bohr notation is a measure of the energy of precession of the orbit round the nucleus. An orbit encircling two nuclei could only precess if the second nucleus moved with it, and the mass makes this impossible. Hence the Bohr system of notation cannot be applied to the orbits of shared electrons. How this difficulty is overcome—how the successive loops, which in an isolated atom cut one another, become, with the shared electrons, superposed—we do not know: it may possibly be due to a correlated oscillation of the nuclei. The attempt to explain it by assuming a figure-of-eight shape for the orbits is not dynamically satisfactory: this may be the correct form of the orbits (or of some of them), but it cannot be made to give the equivalent of the required precession. Whatever the explanation may be, we obviously cannot specify the orbit in terms of its precession when there is none. Hence it is not legitimate to assign quantum numbers on the Bohr system to the shared electrons: we know their quantum numbers before they are shared, but these (or at least one of them) have no meaning after the covalent link has been established. This conclusion disposes of a good deal of argument which has been based on an assumed knowledge of these numbers. Two remarks may be made here.

(*a*) The close similarity in valency properties between successive members of the same periodic group (for example, chlorine, bromine, and iodine) indicates that the capacity of a ' lone ' electron to become shared depends on its second (and third) rather than on its first quantum number: for in these elements the valency electrons have the same second and third quantum numbers, but the first is three in chlorine, four in bromine, and five in iodine.

(*b*) The octet, as we know, is an extremely stable group of electrons, not only when it is unshared (as in the inert gases),

but also when it is completely shared, in four-covalent atoms (further evidence of this will be given later). When it is unshared it consists of $2 \times N_{11}$, $2 \times N_{21}$, and $4 \times N_{22}$ electrons: of these subdivisions the last two resemble one another much more closely than they do the first, so that for many purposes we may divide the group into two subgroups of two and six electrons respectively (this is on the system of Stoner and Main Smith: in the original Bohr theory there were four electrons in each subgroup). In the fully shared octet all that we know is that the eight electrons are in four pairs; there must be some close relation between the orbits of the two electrons of a pair, since they both enclose the same two nuclei, but that is all that we can say of them. There is no indication whatever of any difference between one pair and another, and so it seems very unlikely that the shared electrons can be distributed, like the unshared, into subgroups of two and six. It is more probable that the arrangement of the octet is quite different when it consists of shared electrons.

II. If the shared electron really encircles both nuclei, it must approach each the same number of times per second. Hence the periods of rotation of the subgroups in each atom of which it forms part must agree.[1] Moreover, in a chain of covalently linked atoms this must be true of any two neighbours, and so of the whole chain. It is of course possible that the subgroup which the shared electrons enter is not the same in each atom, and so the periods need not be identical, but they must be rationally related to one another. This suggests a way in which an atom in one part of a molecule may influence all the others, and also gives a condition for the stability of a molecule which may ultimately prove of great importance.

III. In some discussions on covalency it has been pointed out (for example, by Fowler, Sommerfeld, and others) that the hydrogen ion occupies a peculiar position from its small size. So we may suppose that carbon, nitrogen, oxygen, and fluorine complete their octets by taking up 4, 3, 2, and 1 atom of hydrogen respectively: these provide the lacking electrons, and the protons slip into the electron loops, so to speak, without much affecting the structure. This way of regarding the process may be quite sound; but any physical theory founded on it must take account of the fact that whatever a hydrogen atom can do in this way a hydrocarbon radical like ethyl or even phenyl can

[1] See Wilsdon, *Phil. Mag.* 1925, 49, 354, 900.

do likewise. There are of course plenty of differences between the behaviour of a hydrogen atom and that of an alkyl group ; but from the covalency point of view they are equivalent, and a theory of the sharing of electrons must not be made to depend on the small size of the hydrogen ' core ', but must be equally applicable to larger atoms. It is indeed rather remarkable, in view of the great physical contrast between the single proton which forms the core of the hydrogen atom, and the much larger carbon nuclei with their attendant K electrons which the heavier groups possess, that we do not find more differences between a hydrogen compound and its alkyl substitution products. Certain marked differences there are, as in the case of displacement of the hydrogen and its power of co-ordination : but the replacement of one by the other is almost always possible, and it causes less alteration of the properties of the molecule than might on physical grounds have been expected. One of the few marked distinctions would seem to be in the power which hydrogen possesses of forming covalent links by means of a single electron.

One-electron Covalencies.

While in all ordinary cases the evidence is strongly in favour of every covalent link being constituted of two shared electrons, there are a small number of compounds in which it is almost certain that a single shared electron can form a link. The most indisputable of these are two forms of hydrogen. The existence of neutral H_3 has recently been shown to be very doubtful ; but there is no doubt that in positive ray tubes molecules of $[H_2]^+$ and $[H_3]^+$ frequently occur.[1] The first of these has two nuclei and only one electron : the second has three nuclei (and so at least two links) and only two electrons. In each therefore one electron must be able to hold two atoms together. These forms have been described as stable, but this only means that they are formed in fair quantity in the positive ray tube, and appear to persist for the short time that it takes a positive ray to travel along the tube. Being charged molecules they cannot of course be isolated any more than $[H]^+$ can be isolated ; but if they had the stability of an ordinary ion, it should be possible to separate them in the form of neutral compounds with an anion, that is,

[1] Aston has shown that the masses of these are 2·016 and 3·024 respectively.

of salts : we ought to be able to obtain $[H_2]Cl$ and even $[H_3]Cl$, as we can obtain [H]Cl. The fact that such compounds have never been obtained is evidence these molecules with one-electron links are, on the chemical standard, very unstable.

The only other group of compounds in which we must admit the existence of one-electron links is that of the hydrides of boron. There are several of these, all of which agree in containing more hydrogen than can be accounted for on the assumption that boron is trivalent in the ordinary sense. They have been very carefully investigated by Stock, and there is no doubt about their composition and molecular weight. We may take the simplest as an example. This is B_2H_6, a gas boiling at almost exactly the same temperature as ethane. With trivalent boron we should expect B_2H_4. The molecule must have seven links, one between the boron atoms and six to the six hydrogens. Apart from the two K electrons of the boron (the utilization of which for covalency formation would involve an impossibly great expenditure of energy), there are twelve available electrons, six from the hydrogens and three from each boron. It is impossible to account for this except by supposing that two of the hydrogen atoms are attached by one electron each. These compounds are also unstable : they are decomposed by water, they are immensely powerful reducing agents, and they all give off hydrogen either in the cold or on gentle warming.

In addition to their instability all these compounds have this point in common that one of the atoms attached by a single electron is always hydrogen. That this is not an accident is shown by comparing the hydrides with the other compounds of boron. The halides and the alkyl derivatives are all of the type BX_3, and careful investigation by Stock has shown that they give no sign of association to B_2X_6 down to the lowest temperatures, while the hydride has no tendency to dissociate into BH_3 up to the temperature at which it begins to decompose with loss of hydrogen.

We may therefore conclude that the occurrence of links formed of a single shared electron is very rare : that such links are always unstable : and that they are only possible at all when one of the atoms so linked is hydrogen.[1]

[1] The possible existence of a link formed of three shared electrons will be considered under carbon.

Covalency and the Periodic Table.

The conditions which determine whether an atom tends to form ionized or covalent compounds have been discussed by Fajans,[1] whose conclusions are simple and convincing, and strongly supported by experiment. In an ionized molecule it is clear that the electrostatic attraction will bring the ions into close contact, and will distort the orbits of the outer electrons. If we imagine this attraction to increase, the distortion will increase with it, until a point is reached at which the system breaks down : the distorted orbits become less stable than orbits enclosing both nuclei, and the electrovalency goes over into a covalency. The chief factor in determining the change is of course the magnitude of the charge, and that is why the ionization ceases when the valency exceeds a certain value. Further consideration shows that the orbits whose distortion concerns us are those of the negative and not those of the positive ion. These contain the electrons which are ultimately to be shared between the two atoms, and their stability is weakened by the negative charge (and the more so, the larger this is, i.e. the smaller the nuclear charge for a given number of electrons), while that of the cationic orbits is strengthened by the positive charge on the cation. The size of the ions will also be of importance. The smaller the cation is the stronger will be the attraction it exerts on the anionic electrons, and the more likely they are to go over : while with the anion, an increase of size will weaken the stability of its electrons, since they will be further removed from the influence of their nucleus.

We thus arrive at the general conclusions that an electrovalency will tend to pass over into a covalency

(1) When the charge on the ion is large, whether it is positive or negative.

(2) When the cation is small.

(3) When the anion is large.

In applying these conclusions we have to remember that in any periodic group the size increases on the whole with the atomic number, but that (especially in the earlier groups) the ions of the B subgroup are much smaller than those of the A. Hence we should expect to find that ionization was in general greatest among the elements of lower valency : that with the metals it

[1] Fajans and Joos, *Z. f. Phys.* 1924, **23**, 1 ; Fajans, *Naturwiss.* 1923, **11**, 165 ; *Z. f. Krystallogr.* 1925, **61**, 18.

was more marked in the heavier than in the lighter members of a group, and more in the A than in the B subgroup :[1] while among the electronegative elements it should be more prevalent among the lighter than among the heavier atoms.

It remains to see how far these principles are confirmed by observation. We have several methods for determining the tendency of molecules to ionize under various conditions. There is the obvious test of ionization in water, the indications given by the volatility, the work of Biltz on the electrical conductivity of the pure fused chlorides, and the results of Grimm and Sommerfeld, based on the crystalline structures.

Biltz [2] collected the data as to the conductivities of a large number of pure chlorides just above their melting-points, most of which he had measured himself. The results are complicated by the fact that they have to be measured over a very wide range of temperature, since the compounds must be in the liquid state. The conductivity always increases with the temperature, but to very varying extents ; and, except that the temperature coefficient is greater the smaller the absolute conductivity, we do not know what this correction amounts to, and so we cannot make allowance for it. We must take the results as they stand, as depending both on the tendency of the compound to ionize, and on the height of its melting-point. Since the melting-points of ionized compounds are always higher than those of covalent compounds, this has the result of exaggerating the natural differences in conductivity, and dividing the compounds very sharply into two classes ; but the conductivities vary over so large a range (in the ratio $1 : 10^8$) that the temperature effect is in comparison almost negligible. Out of 60 chlorides of 53 elements examined 31 were found to have conductivities lying between 10 and 0·1 (ohm^{-1} cm. at the melting-point) while for 26 the value was less than 2×10^{-6}. Only 3 came within these wide limits : $BeCl_2$, 0·0032 at 451°, $ZnCl_2$, 8×10^{-4} at 318°, and $HgCl_2$, $0{\cdot}8 \times 10^{-4}$ at 277°.[3]

The work of Grimm and Sommerfeld [4] has already been mentioned. They deal only with compounds of the general formula

[1] There is evidence that apart from the difference in size cations of inert gas numbers have less effect than others in deforming anionic orbits.

[2] *Z. anorg. Chem.* 1924, **133**, 312 ; Biltz and Klemm, ibid. 1926, **152**, 267.

[3] $HgBr_2$ (0·0015 at 235°), HgI_2 (0·012 at 252°), and InI_3 (0·054 at 210°) have similar intermediate values.

[4] *Z. f. Phys.* 1926, **36**, 36.

AB, in which therefore if A is from the Nth periodic group, B is from the (8 − N)th (IV, IV : III, V : II, VI : I, VII), and regard them as ionized when they have either a rock salt (6 : 1) or caesium chloride (8 : 1) lattice, and covalent when they have a diamond (4 : 1) or wurtzite (4 : 1) lattice. It is uncertain whether they are justified in drawing so absolute a conclusion : various objections can be raised to it, especially that some of the elements of the fourth group (which they include as being so to speak of the AA type of formula) such as tin, crystallize in a diamond lattice and yet have a considerable conductivity (at any rate in comparison with the almost completely insulating diamond), which would seem to suggest ionization. However, their conclusions may be given : they certainly fall into line with the rest of the evidence. They involve the assumption, for all compounds except those of elements of the fourth group, of a transference of electrons by a sort of co-ordination. In zinc sulphide (wurtzite), for example, we must suppose that the sulphur gives up two electrons to the zinc, so that each atom has four, like carbon and silicon, enabling the compound to form a giant molecule of four-covalent atoms like carborundum : the formula of the ionized form being $[Zn]^{++}S^{--}$, that of the covalent should be written $(Zn^{--}S^{++})_n$. The evidence of the intensities of the X-ray reflections certainly does not disprove this, though it may be doubted whether it is of great value in supporting it.

The evidence available from these various sources as to the tendency of the elements to form ions may be summarized under the various periodic groups.

Group I A. (Alkali metals, the largest cations, with the smallest charge.) Their compounds, such as the halides, are always ionized under all conditions.

Group I B. Cuprous chloride and silver halides are ionized in water (so far as they dissolve). The crystal structure of cuprous chloride, bromide, and iodide are all of the diamond type ; silver iodide crystallizes both in the diamond and in the wurtzite forms, but the bromide and chloride in the sodium chloride form. Here the much smaller cations have a stronger tendency to form covalencies, and this is more marked in copper, because it is the smaller of the two. In the fused state, however, both cuprous and silver chlorides are ionized.

Group II A. The salts of the typical and A elements are all ionized in water : all the chlorides are good conductors

except that of beryllium. Magnesium oxide and the sulphides of magnesium, calcium, strontium, and barium are all of the rock salt type. But beryllium, which is much the smallest, gives an oxide of the wurtzite type, and its chloride is a poor conductor.

Group II B. These elements all show a very limited power of ionization. Cadmium chloride is imperfectly ionized in water, and mercuric chloride is definitely a weak electrolyte. Of the fused salts also the conductivities are low, and that of mercuric chloride very low (the tendency of mercury to assume the covalent form is quite exceptional, and must be due in part to causes outside the Fajans theory). Zinc oxide (but not cadmium oxide) and the sulphides of all three metals have covalent lattices.

Group III A. Boron shows no signs of ionization by any test. Aluminium chloride is ionized in water, but not in the fused state, as the volatility and absence of conductivity show. Its nitride AlN has the wurtzite structure. Scandium chloride is ionized in water and in the fused state, and its nitride ScN has the rock-salt structure. Yttrium and lanthanum chlorides are good conductors when fused. The progress of ionization with increase in atomic number is very marked in this group.

Group III B. The chlorides of all these elements, so far as they can be measured, are good conductors when liquid : $GaCl_3$, $InCl_3$, $InCl_2$, InCl, TlCl ; $TlCl_3$ appears to decompose when melted.

Group IV : typical and B elements. All their chlorides of the type XCl_4 (C, Si, Ge, Sn, Pb) are non-conductors in the liquid state.

Group IV A. $TiCl_4$ is a non-conductor in the pure state : the other chlorides cannot be measured. The carbides of titanium and zirconium are, however, of the rock salt type.

Grimm and Sommerfeld have included in their investigation the free elements of the fourth group, which may be regarded as 1 : 1 compounds of the element with itself. They find that all the typical and B elements with the exception of lead, whose structure is imperfectly known, have the diamond structure, but that all the A elements (Ti, Zr, Ce, Hf, Th) have a close-packed structure.

This concludes the list of elements which can form cations, and it will be seen that the theory of Fajans is entirely confirmed.

The same is true of the formation of anions, though the evidence is less full, since we are concerned only with the halogens and the oxygen-sulphur group. Here, according to Fajans, we ought to find that size has the opposite effect : the smallest and lightest atoms should show the greatest tendency to ionize.

We have already seen that the boiling-points indicate that with certain elements the fluorides are ionized while the other halides are not. This difference is very marked with the compounds HgX_2, AlX_3, and SnX_4, and indications of it are found with ZnX_2, CdX_2, SbX_3, TiX_4, GeX_4 (X = halogen). The crystallographic data confirm this conclusion. Silver iodide has a diamond and wurtzite lattice (in the two forms) while the fluoride, chloride, and bromide all have ionic lattices. In the same way among the elements of Group VI cadmium oxide has an ionic and cadmium sulphide a covalent lattice.

VII

CO-ORDINATION

WE have adopted the term 'co-ordinate' to describe those covalencies in which both of the shared electrons are derived from the same atom, since it is the recognition of this form of linkage which makes it possible to reconcile the theory of co-ordination, by which Werner was able to throw so much light on the behaviour of inorganic compounds with that of structural chemistry. We may therefore briefly consider the new ideas of molecular structure which Werner introduced, and the way in which the electronic theory is able to interpret them.

Werner's Theory of Co-ordination

This theory, which was first suggested in 1891, and developed more fully in 1893,[1] originated in an attempt to explain the structure of a series of so-called 'molecular' or 'complex' compounds formed by the combination of apparently saturated molecules, and especially of those which many salts form with ammonia. The attempts which had been made to give structural formulae to these (often very stable) compounds were admittedly unsatisfactory. Werner proposed an entirely new principle of molecular structure: that it was (at least largely) determined by the tendency of certain atoms to attach to themselves a definite number of other atoms or groups, irrespective of whether these were univalent atoms or groups, or whole molecules capable of independent existence. This number he called the 'co-ordination number': every atom had a maximum co-ordination number, usually six or (less often) four, although it could also form 'co-ordinatively unsaturated' molecules, in which this number was not reached. In addition to the atoms or groups of this co-ordination complex, which were said to occupy the 'first sphere', the molecule might contain other atoms or groups less closely attached in a 'second sphere': these did not count

[1] Alfred Werner, 'Beiträge zur Theorie der Affinität und Valenz', 1891: *Z. f. anorg. Chem.* 1893, 3, 267. This latter paper contains the essential principles of the theory, which were not seriously altered, although they were very greatly developed, in his 'Neuere Anschauungen auf dem Gebiete der anorganischen Chemie', of which the first edition appeared in 1905, and the last in his lifetime (he died in 1919) in 1913.

towards the co-ordination number. For example, in the hexamine of cobaltic chloride $[Co(NH_3)_6]Cl_3$ the ammonia molecules were regarded as occupying the first sphere of the cobalt and satisfying its maximum co-ordination number 6, while the chlorine atoms occupied the second sphere. Experimentally the groups in the outer sphere were characterized by being ionized in water, while those constituting the co-ordination group were not. To mark this distinction Werner introduced the square bracket [ ] to enclose the atoms which formed the co-ordination complex and were not ionized. This symbol was an essential part of the theory, and he was careful to justify the position he assigned to it by experimental determination of the degree and nature of the ionization. To allow of the attachment to the central atom of more groups than the ordinary valency permitted, Werner adopted the idea of subsidiary valencies, indicated by dotted lines to distinguish them from the ordinary valencies ; this part of the theory however need not detain us : it was ultimately admitted, if not by Werner at least by his successors, that within the co-ordination group when once it was constituted, this distinction vanished, and all the valencies attaching the groups to the central atom were identical.

Werner assigned definite positions in space to the groups in a co-ordination complex.[1] Where there were 4, an arrangement at the points of a tetrahedron had already been established for carbon by van 't Hoff ; but Werner showed that a different arrangement must occur in the 4-co-ordinated compounds of platinum : these are never optically active, but those of the type Pta_2b_2 occur in two (geometrically) isomeric forms, which is possible if the four groups are in the same plane with the central atom, but not if they occupy the corners of a tetrahedron. To the groups in a 6-co-ordinated complex he assigned the simplest distribution in three dimensions, at the points of an octahedron, and justified this by showing that certain compounds which on this assumption must have asymmetric molecules, could be resolved into optically active forms.

This conception of the fundamental importance of the co-ordination number—the number of groups joined to the central atom by non-ionized links, whether these are univalent groups or whole molecules—is the kernel of the Werner theory. But observation of the properties of these compounds disclosed another conclusion of equal generality. This is apparent if we

[1] For further details see Chapter XII.

compare the formulae of any particular series of compounds such as those formed by the combination of platinic chloride with ammonia. In the following list the position of the square brackets has in every case been determined by experiment. Under each formula is given the molecular conductivity at 25° and V =1000 : this is roughly proportional to the number of ions into which the molecule dissociates in solution :

$[Pt(NH_3)_6]Cl_4$ 523 $[Pt(NH_3)_5Cl]Cl_3$ 404 $[Pt(NH_3)_4Cl_2]Cl_2$ 229

$[Pt(NH_3)_3Cl_3]Cl$ 97 $[Pt(NH_3)_2Cl_4]$ 0 $[Pt(NH_3)Cl_5]K$ 108·5

$[PtCl_6]K_2$ 256

The co-ordination number is 6 throughout : the platinum atom always has six groups (NH_3 or $-Cl$) attached to it by non-ionized links. But there is the further remarkable fact that whenever a whole molecule of ammonia is replaced within the complex by a univalent group (Cl), the complex loses one positive charge, its electrovalency falling by one if it is positive, and rising by one if it is negative.

Platinous chloride gives a similar series of ammines, but in these the co-ordination number is four. They behave in exactly the same way :

$[Pt(NH_3)_4]Cl_2$ 260 $[Pt(NH_3)_3Cl]Cl$ 116 $[Pt(NH_3)_2Cl_2]$ 0

$[Pt(NH_3)Cl_3]K$ 107 $[PtCl_4]K_2$ 267

This characteristic change of electrovalency is universal in all these series of compounds, whether the central atom is platinum, cobalt, chromium, or another metal : and whether the attached groups are on the one hand ammonia, water, or other molecules, or on the other hand chlorine, bromine, NO_2, or other univalent groups.

The fundamental points in Werner's theory thus are (i) the importance of each central atom being attached by non-ionized links to a definite number—usually six, less often four—of other atoms or groups, this number having no relation to the periodic group of the central atom ; (ii) the fact that these groups may

either be univalent atoms or radicals, or whole molecules; and (iii) the universal change in the electrovalency of the compound when a group belonging to one of these types is replaced within the complex by one of the other type.

Werner maintained that the undeniable successes of the theory of structural chemistry in dealing with organic compounds were due to its being, in the special case of carbon, in many ways identical with the co-ordination theory, because carbon was in the unique position of having a valency identical with its maximum (and usual) co-ordination number—a remark which, as we shall see, goes far to explain the exceptional position of carbon. To the ordinary chemist it appeared that Werner had not succeeded in dethroning structural chemistry so far as organic compounds were concerned, but that he had provided a new theory of structure which was of great value in accounting for the behaviour of inorganic compounds, especially of those complex or 'molecular' compounds with which the old structural theory had proved itself incompetent to deal.

This was clearly an unsatisfactory position; it represented molecules as being built on two different and apparently irreconcilable plans, and it emphasized an obviously false distinction between organic and inorganic chemistry. The conflict could only be temporary: it must ultimately be resolved by the discovery of a more complete theory of valency, of which the structural theory and the co-ordination theory would prove to be partial aspects. The solution was provided by the electronic theory, with the recognition of the third type of linkage, a covalency in which both electrons are supplied by the same atom.

Electronic Interpretation of Co-ordination [1]

In the first place it is clear that the links which join the units of a co-ordination complex to the central atom are covalent. This is really self-evident if our theory is true, since Werner showed that they were not ionized, and a covalent link is the only alternative which we have admitted; but it is established conclusively by the final tests of geometrical and optical isomerism. Hence the maximum co-ordination number is the maximum covalency number: an atom with a co-ordination number of six is one which can form six covalencies, and so can have a valency group of twelve shared electrons. We have already

[1] See Sidgwick, *J. C. S.* 1923, 123, 725.

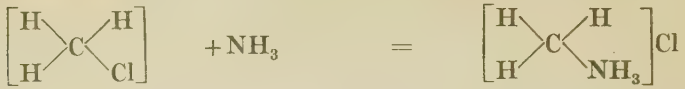
seen that this is possible, and that it occurs in such compounds as SF_6 and $K_2[SiF_6]$. Similarly a co-ordination number of four implies a valency group of eight, which of course is the most familiar form. So far there is nothing involved in the co-ordination theory which we have not already accepted. The attachment of a univalent radical like chlorine or NO_2 is a covalency of the normal type, to which the radical in question supplies one electron, and the central atom the other. But an independent molecule like water or ammonia must already have an even number of valency electrons, and so cannot form its linkage in this way: if it had a single odd electron available for the purpose, or if it could accommodate one further electron borrowed from the central atom, it would not be able to exist by itself; it must attach itself by sharing with the central atom a lone pair of its own electrons—in other words, by forming a co-ordinate link. All the molecules capable of entering into a complex in this way can be shown to have the necessary lone pair: the nitrogen in ammonia has one such pair, and the oxygen in water has two. Thus the number of shared electrons in the valency group of the central atom will be the same whether the co-ordinated units are molecules or univalent radicals, and this explains why those of one kind can replace those of the other unit by unit, as they are found to do.

The characteristic change of electrovalency which accompanies such a replacement necessarily follows. Suppose we start with the non-ionized compound $[Pt(NH_3)_2Cl_4]^\circ$. If a (neutral) chlorine atom is removed, it will take with it one of the electrons which it previously shared with the platinum, but will leave the other behind. If now an ammonia molecule takes its place, this provides the two electrons required for its attachment, so that the platinum has gained one electron by the exchange. Since it must in the original compound have had the number of electrons required for stability, it now has one too many: it will lose this, and thereby acquire a positive charge, appearing as a cation in the salt $[Pt(NH_3)_3Cl_3]Cl$. The process can be represented by the scheme:

$$[Pt^{\times}_{\cdot}Cl]^\circ \longrightarrow [\dot{P}t^{\times}]^\circ \longrightarrow [Pt{:}NH_3]^\circ \longrightarrow [Pt{:}NH_3]^+$$
$$\times$$

This change of electrovalency on replacement is not peculiar to the Wernerian complexes. There is a very familiar example in organic chemistry, though it is not usually formulated in this way. When ammonia acts on methyl chloride, methylamine

hydrochloride is formed : the chlorine is replaced by NH_3, and the electrovalency of the complex changes from zero to +1 : [1]



This suggests another way in which the reaction may equally well be described. The nitrogen of the NH_3 in the complex is quadrivalent : it is in the form of a substituted ammonium, with all the rest of the complex as substituent. In order to become quadrivalent nitrogen must, as we know, lose an electron. Hence we may say that a neutral chlorine atom is first removed from the central atom ; the ammonia molecule then gives up an electron to the chlorine, converting it into chlorine ion, and the resulting positively charged univalent radical $[-NH_3]^+$ takes the place of the chlorine, carrying its positive charge into the complex.

The position is perhaps made clearer (and the formulae are certainly easier to remember) if we consider how many electrons the central atom has gained or lost by forming the complex. Every molecule (as NH_3) added gives it two : every univalent radical gives it one : further, the electrovalency of the complex must be added if it is negative, and subtracted if it is positive. Thus we have

$[PtCl_6]^{--}$	$+6+2$	$= 8$
$[Pt(NH_3)Cl_5]^-$	$+2+5+1$	$= 8$
$[Pt(NH_3)_6]^{++++}$	$+2\times6-4$	$= 8$

It will be seen that all the 6-co-ordinated platinum compounds whose formulae are given on p. 111 show in this way a gain of eight electrons. Similarly the 4-co-ordinated compounds of platinum all show, like $[Pt(NH_3)_4]Cl_2$ $(2\times4-2 = 6)$, a gain of six. These numbers, which may perhaps be called the ' effective valencies ' of the central atom, are characteristic for each particular series of compounds : thus for the ammines of trivalent cobalt and chromium the number is nine, as in $[Co(NH_3)_6]Cl_3$ $(2\times6-3)$.

Werner's theory was not limited to the peculiar addition compounds which we have been considering, and with which his name is especially connected. He applied it in great detail to

[1] Ramsay gave a very similar explanation of this reaction in 1908 (*J. C. S.* 93, 785).

the whole of chemistry—more particularly inorganic chemistry—and throughout his applications it is found that the electronic interpretation of his theory holds good. It is thus clear that there is no real opposition between the Werner theory and that of structural chemistry. The same electronic principles can be applied to both : they are different aspects of the same process, the former recognizing the existence of these peculiar co-ordinated compounds which the latter, in its classical form, disregards ; and the reason why the structural theory, in spite of disregarding them, has been of so much service in organic chemistry is very largely that suggested by Werner, that carbon, having the number of valency electrons required to give it directly its maximum covalency of four, seldom if ever forms co-ordinate links. Other elements often do so, and hence structural chemistry could not deal with them satisfactorily until it had taken co-ordination into account.

This interpretation breaks down the supposed distinction between organic and inorganic chemistry which the opposition of these two theories had suggested. It also removes an apparent weakness in the Werner theory, that it seemed to attribute a unique character to one atom in the molecule, as the ' centre of co-ordination '. It is now evident that this is merely an arbitrary distinction, a matter of convenience. Every atom in the molecule is a centre in the same sense, though some will have a higher co-ordination or covalency number than others. Every atom has a valency group of electrons made up by the same processes to a stable number, and the molecule owes its existence to this stability.

There are many sides of Werner's theory which have not yet been touched upon. One of the most valuable is the fundamental importance which he ascribes to the co-ordination number, that is, as we now understand it, to the number of shared electrons ; this is in complete agreement with the electronic theory, but could scarcely have been deduced from it ; and in recognizing its importance, Werner undoubtedly made a great advance in our knowledge of the principles of molecular structure. This question, together with the equally important one of the relation between this number and the structure of the atom, will be more fully discussed in Chapter IX. Other aspects of the theory will naturally arise later. Any discussion of molecular structure involves frequent reference to the conclusions of Werner, whose insight into such problems was extraordinarily acute.

Conditions of Formation of Co-ordinate Links

When a co-ordinate link is formed between two atoms, one of them gives the other a share in two of its own (previously unshared) electrons :

$$A + :B \longrightarrow A:B \quad (A \leftarrow B).$$

It is therefore of the essence of this type of link that, unlike a normal covalency, it requires for its formation two atoms of different characters : this distinction, which was not apparent in Werner's theory, is of fundamental importance. In order to express these two functions, we may call the atom which lends the two electrons (A above) the *donor*, and the one which receives them (B) the *acceptor*. A necessary condition for the donor is that it should possess a lone pair of valency electrons : a ' covalently saturated ' molecule like CH_4 or C_5H_{12} cannot provide a donor, because all its valency electrons are already shared. This condition is of course not sufficient (an atom which has a lone pair may refuse to act as a donor), because the product may be unstable ; but the same may be said of any of the general conditions of chemical combination. In forming the link, the donor does not change the number of its valency electrons, while the acceptor increases its own number by two. Hence if the valency group of the donor is of a stable size after co-ordination, it must have been so before : the donor must have formed part of a stable molecule. This was the fundamental problem which Werner had to solve, that molecules apparently saturated still had the power of further combination. The acceptor, on the other hand, must have room in its valency group for two more electrons. This may arise in four different ways.

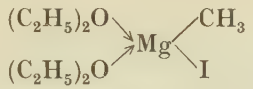
(1) The acceptor may be a truly unsaturated isolated divalent atom, as of oxygen or sulphur, having only six valency electrons to start with :

$$(C_2H_5)_3N + O \longrightarrow (C_2H_5)_3N \rightarrow O.$$

In such compounds the co-ordinate link is exceptionally strong, because if it breaks the acceptor fragment is highly unstable. Links of this kind always appeared in the older formulae as double bonds as in $(C_2H_5)_3N=O$.

(2) It may have an incomplete ' octet ' of shared electrons, as in $Mg(CH_3)I$, where the magnesium has four, or in BCl_3, where the boron has six shared electrons : such imperfect valency

groups, when they are all shared, are not too unstable for the molecule to exist. Examples of the products of co-ordination of such atoms are the compound of boron trichloride and ammonia $H_3N{\rightarrow}BCl_3$, and the Grignard reagent:



(3) A stable cation like Na^+ or Zn^{++}, although it has a complete (unshared) outer group (which may or may not be called a valency group) of eight or eighteen electrons, can take up another complete and wholly shared valency group of eight or more. The positive charge on the cation will promote the co-ordination, as it increases the tendency to borrow negative electrons. The factors indicated by Fajans as assisting the formation of covalencies—the influence of the magnitude of the charge and the size of the ion—will of course be important in such a case. (It may be pointed out that the elements which form particularly stable ammines, such as the transition elements, have a very small atomic volume, as Fajans' theory requires.) It is this process which leads to the hydration of ions in solution, and in the solid salt.

(4) Since the octet is not the only form of stable group, but can expand with some atoms to twelve or even sixteen electrons, an atom with a completed octet may act as an acceptor by increasing its valency group. Thus we have the reaction

$$SiF_4 \longrightarrow K_2[SiF_6],$$

where the silicon forms links in this way with two fluorine ions, its octet expanding to twelve.

Under this head must be included hydrogen, of which the valency group is normally two, but can, as we have seen, be increased by co-ordination to four. The question of the conditions which make such an increase possible (either with hydrogen or with other atoms) is of great interest, but as yet no general answer can be given to it. With hydrogen, co-ordination only occurs readily if it is in a hydroxyl group (water, alcohols, phenols, acids), or is attached to fluorine (in H_2F_2); when the hydrogen is attached to nitrogen, as in the amines, it can occur, but much less easily; with hydrogen attached to carbon it is almost unknown.

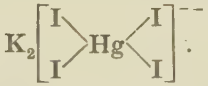
These are the general conditions of formation of co-ordinate links. There are two classes of co-ordinated compounds which

are of special importance and may be mentioned here, double salts and chelate compounds (the still more important class of associated substances is discussed in the next chapter).

Double Salts

It cannot always be assumed that a ' double salt '—a solid phase whose composition can be expressed as the sum of an integral number of simple salt molecules of more than one kind (with or without solvent molecules)—really contains a complex molecule; there is always a possibility that it is only a crystalline aggregate of simple salt molecules. It is an experimental question, which in general can only be decided by determining whether the complex exists in solution, although in some cases the X-ray evidence of crystal structure may be sufficient. Proof that dissociation into the components occurs in solution is not decisive against the existence of the complex, unless the dissociation can be shown to be complete: many true complex salts, like the fluosilicates, are considerably dissociated in this way. Where however the complex exists, the mechanism of its formation is simple. Suppose we start with salt MX_m (X = univalent radical). In the non-ionized form the metal M is exerting m covalencies. If this forms a complex salt with n molecules of, say, an alkaline salt BX, the M atom (as acceptor) forms co-ordinate links with n more X ions: this gives it n negative charges, which are neutralized in the separated salt by n B^+ ions, giving the complex salt $B_n[MX_{m+n}]$, in which the atom M has a covalency of $m+n$. Thus mercury in the covalent form of mercuric iodide I–Hg–I has a valency group of four shared electrons, two from the mercury and one from each of the iodine atoms. In presence of potassium iodide it can co-ordinate with another iodine: this was originally an ion, with its octet completed by the transference of an electron from a potassium atom: it lends two electrons to the mercury, which becomes 3-covalent, and the complex has the negative charge due to the iodine ion: this gives $K[HgI_3]$. The same process can occur again, giving a complex with two negative charges and a 4-covalent mercury atom, in $K_2[HgI_4]$. The reaction may equally well be represented by saying that the mercury acquires the two electrons necessary for its new covalency, one from the potassium and the other from the (neutral) iodine. The formula of the resulting salt must always be the sum of those of a few molecules of the components. As we have seen, it is

idle to ask whether the linkage of the X groups to the central atom is normal or co-ordinate. If we imagine the reaction to be directly between the mercuric iodide and an iodine ion we should call it co-ordinate : if the potassium is supposed to transfer an electron to the mercury, and so make it trivalent and capable of combining with another (neutral) iodine atom, we should call it normal. But if we wish to call the link co-ordinate we must not write it Hg←I, which would imply that a neutral iodine atom with seven valency electrons had lent a pair to the mercury, but Hg←$[I]^-$, since it is only an ion which could form the linkage by co-ordination. If the latter formula means anything that $[Hg{-}I]^-$ does not, it implies that the whole of the negative charge resides on the iodine atom, an assumption for which there is no justification. In the complex there is no difference between the linkage of the first two iodine atoms of the HgI_2 and that of the others : the molecule, if it is to be written in full, is

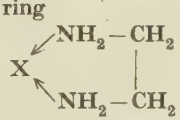


It has however this in common with other co-ordinated compounds, that it can break up comparatively easily into its components potassium iodide and mercuric iodide, since these are both stable molecules.

Chelate Compounds

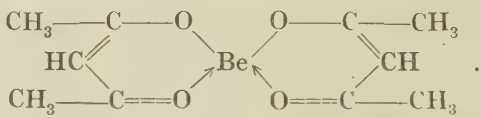
In the compounds we have so far discussed, the donor and acceptor originally formed part of two separate molecules. It is however equally possible for co-ordination to take place between two atoms which already form part of the same molecule. In that case the product must contain a ring, and such substances have been called by Morgan by the convenient name of ' chelate ' compounds.[1] Their existence was for a long time unrecognized,

[1] From χηλή, a crab's claw (Morgan and Drew, *J. C. S.* 1920, **117**, 1457, note). Professor Morgan applies this term to all rings containing co-ordinate links, and so includes, for example, Werner's ethylene diamine (en) compounds, with the ring



From our point of view, those with only one such link in the ring are of more interest.

since the molecule could be represented as an open chain without assuming a co-ordinate link : the discovery of their nature was due to Werner. They are a peculiarly stable group of compounds, probably because the normal covalencies hold the molecule together even if the co-ordinate link breaks. The most remarkable are the metallic derivatives of the β-diketones, and especially of acetylacetone. These diketones are definitely though not strongly acidic, and evidently react in the enolic form, as $\begin{matrix} CH_3{-}C{=}CH{-}C{-}CH_3 \\ \quad\;\; | \qquad\quad \| \\ \quad OH \qquad O \end{matrix}$. This substance, acetylacetone, forms compounds with a surprisingly large number of elements (over sixty), in which an atom of the element replaces the hydroxylic hydrogen in one or more molecules of the ketone, according to the ordinary rules of valency. Thus if we write A for the radical $C_5H_7O_2$ remaining when this hydrogen is removed, we have such compounds as NaA, BeA_2, AlA_3, ZrA_4. These were originally (and naturally) assumed to be salts. A few, such as those of the alkali metals, actually are salts and behave as such, but the majority have quite different properties. They have low melting-points and are volatile, sometimes without decomposition at atmospheric pressure : they dissolve readily in hydrocarbons, and only slightly in water, in which they give non-conducting and non-hydrolyzed solutions. All these properties show that the compounds are not ionized but covalent. The formation of these derivatives is common to β-diketones in general (and to many β-keto-esters as well), but it does not occur with α- or γ-diketones : the position of the second oxygen atom evidently determines the formation. Werner pointed out that this could be explained by supposing that the metal formed a co-ordinate link with this second oxygen, with the production of a ring. Thus we should write the beryllium compound of acetylacetone



The metal is not ionized. It has a fully shared octet, two of its covalencies being normal, and the other two co-ordinate. This explains the peculiar non-polar character of these compounds, which led to the detection of their structure.[1]

[1] The properties of chelate compounds are considered in more detail in Chapters IX and XIII.

Properties of the Co-ordinate Link

The peculiar properties conferred on a molecule by the presence of a co-ordinate link depend on two characteristics: (1) that this link is in general more easily broken than an ordinary covalency; and (2) that it involves an electrostatic disturbance in the molecule, and consequently a stronger external field. The weakness of this link, which is shown by the ease with which an addition compound often breaks up again into its component molecules, has led to the belief that it is due to an affinity of an inferior order to that of ordinary 'valency' links—possibly to an attraction between whole molecules much weaker than that which holds together the atoms in each molecule. Even after Werner had recognized that the forces were always from atom to atom and not from molecule to molecule, the use of such terms as subsidiary valency or residual affinity seemed to countenance the idea that these links were somehow not quite genuine valencies. If we are to maintain that the mechanism of a co-ordinate link is the same as that of a normal covalency, some explanation must be given of the undoubted fact that it is usually easier to break. The explanation is simple. The work required to break a link—that is, to separate a molecule into two parts—is the difference between the energy-content of the molecule and that of these parts. Hence the more unstable the resulting fragments, the more difficult the link is to break. Now, as we have seen, it is characteristic of the great majority of co-ordinate links that they are formed between atoms previously belonging to more or less saturated molecules. The complex can therefore break up again into these two molecules, the loaned pair of electrons returning to its former place; and for this rupture comparatively little energy is required. But the normal covalency cannot do this. If it breaks, it forms two unsaturated univalent radicals ('odd molecules') which are very unstable, that is, have a high energy-content. It tends therefore to be more stable. It is indeed possible for a normal covalency to break in another way without giving 'odd molecules': instead of one of the two shared electrons going away with each half, they may both go with one. In that case the products are ions:

The recombination of ions to form a covalent molecule is in fact a kind of co-ordination. But it is only under particular

conditions that the parts of a molecule can exist as ions ; and when these occur the covalency is of course easily broken.

This view of the cause of the weakness of co-ordinate links in general is confirmed by the fact that one type of co-ordinate link is not weak, that in which a neutral divalent atom with a valency sextet acts as acceptor (type (1), p. 116). In the amine-oxides, or such compounds as sulphuric acid, the co-ordinate link to the oxygen is as stable as a normal covalency, the reason being that the product of its rupture, an isolated oxygen atom, would be as unstable as an ordinary univalent radical. The weakness of co-ordinate links in general is therefore a necessary consequence of the conditions of their formation.

It is evident that some disturbance of electrostatic balance must accompany the formation of a co-ordinate link. If the two molecules between whose atoms the link is formed were originally neutral, the acceptor must receive a certain amount of negative charge, since it gains a share in two new electrons, and the donor must receive an equal positive charge. If we assume that the electrons are shared equally between the two atoms, each will count as a half for each atom ; the acceptor will receive a charge of -1 unit, and the donor of $+1$ unit. But this implies that the electron spends an equal amount of time with each of the two atoms, which it cannot be assumed always to do. There must in fact be some electrostatic disturbance even in a normal covalency (unless the two atoms are the same, as in H–H or Cl–Cl), and this must be subtracted from (or added to) the primary disturbance of one unit caused by a co-ordinate link. Every atom, even that of a monatomic gas like argon, has a certain external field ; it is this which gives rise to the factor a in the van der Waals equation, and which determines the volatility. If there were no such field liquefaction would be impossible : if it were constant in intensity we should expect that compounds of the same molecular weight would boil at the same temperature. But we find that this is not so, and that the molecules of compounds—even the least ' polar '—show signs of a stronger external field than those of elements. Argon (mol. wt. 40) boils at $-186°$ C., and oxygen (32) at $-183°$, whilst ethane (30) and even methane (16) have higher boiling-points of $-88°$ and $-161°$. Hence a compound molecule has an increased external field, owing no doubt to the unequal distribution of the linking electrons between the dissimilar atoms which share them. The primary assumption that the donor in

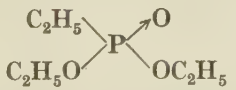
a co-ordinated molecule has a charge of +1 unit is therefore subject to an uncertain correction. But this correction is evidently small, and the external field must be much increased by the presence of co-ordinate links. This conclusion is supported by the properties of substances containing these links, and especially by their diminished volatility and their increased dielectric constant.

(1) *Volatility.* As we have seen, the large external field of ionized molecules diminishes the volatility by holding the molecules together. A similar but smaller effect is to be expected with co-ordinated molecules. The best test of this is to compare isomeric compounds, of which one contains a co-ordinate link and the other does not. The number of available instances is small (in order to avoid possible complications associated liquids are excluded), but it is sufficient for our purpose. A good example is given by the nitro-compounds $R-N\langle^{O}_{O}$ and the nitrous esters R–O–N=O.

Boiling-points at 760 mm.

Formula.	*Nitro-compound.*	*Nitrite.*	*Difference.*
CH_3NO_2	101°	−12°	113°
$C_2H_5NO_2$	114°	+17°	97°
$C_4H_9NO_2$	152°	75°	77°

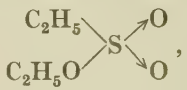
The difference caused by the co-ordinate link naturally diminishes as the molecule grows larger. The aromatic nitro-compounds have similarly high boiling-points; there are no isomeric nitrites with which to compare them, but this is shown by the fact that nitrobenzene (mol. wt. 123) boils at 208°, while chlorobenzene (mol. wt. 112·5) boils at 132°, and bromobenzene (157) at 155°. The diethyl ester of ethyl-phosphonic acid



boils at 198°, and the isomeric triethyl phosphite $P(OC_2H_5)_3$ 42° lower, at 156°. The amine oxides show the same peculiarity in a marked degree. Trimethylamine oxide $(CH_3)_3N\rightarrow O$ is a solid which decomposes without melting at 180°, while the isomeric trimethylhydroxylamine $(CH_3)_2N\cdot O\cdot CH_3$ boils at 30°, and $(CH_3)C_2H_5N\cdot O\cdot C_2H_5$ at 79°.

(2) *Dielectric Constant.* This is a measure of the work done by an external electric field in orienting the molecules against the

effect of their thermal agitation. Its magnitude therefore depends on the moment of the molecules as dipoles, that is, as containing an excess of positive electricity at one part, and of negative at another : it thus measures the extent to which the electrostatic balance is displaced. While the value of the dielectric constant is for hydrocarbons about 2–3 [1] (being less for the paraffins than for the benzene series), for ethers about 4, and for esters about 7 (all these being free from co-ordinate links), we find that for nitromethane it is 39 [2] and for nitrobenzene 36. A striking example is given by the two forms of diethyl sulphite : for the true sulphite $(C_2H_5O)_2S\rightarrow O$, with one co-ordinate link, the dielectric constant is 16, while for the isomeric ethyl ester of ethyl-sulphonic acid



with two such links, it is 42.

In these examples also I have avoided quoting any associated liquids, as they have peculiarities of their own, and will be discussed in the next chapter.

Molecular Volume : Sugden's Parachor

Another property which we should expect to be affected by the intermolecular attraction caused by the external field of a co-ordinated molecule is the volume. As an electrovalency leads to a smaller molecular volume than a normal covalency a similar effect should be produced by a co-ordinate link ; but the effect would not be large, partly because the electrostatic disturbance is smaller, but mainly because the co-ordinated group is still held in its position by the shared electrons, and close-packing is impossible. Hence the effect could not be discovered without an accurate means of calculating the contribution of each atom to the molecular volume. Until recently no such means was available. The work of Kopp, Traube, and others detected certain regularities in molecular volume, but the constitutive

[1] The value depends on the temperature, and on the frequency of the electromagnetic waves employed for the measurement ; but these factors are of subordinate importance, and do not affect the order of magnitude.

[2] In tetranitromethane $C(NO_2)_4$ it falls to 2·3, which is about the value for a hydrocarbon. This must be due not to the absence of co-ordinate links (of which there is one in each nitro-group), but to their symmetrical distribution in the molecule.

element was so large and uncertain that no very detailed conclusions could be based on the results. Even the conditions of measurement were not agreed upon : Kopp measured his molecular volumes at the boiling-point, and Traube at a fixed temperature ; and in neither way were the substances in strictly comparable states. The question has been put on a firmer basis by the work of Sugden.[1] He pointed out that in calculating the molecular volume allowance should be made for the effect of the very large internal pressure of liquids, which is manifested in the surface tension. It has been shown that for a non-associated liquid the influence of temperature on the surface tension is given by the expression $\frac{\gamma^{\frac{1}{4}}}{D-d}$ = constant, where γ is the surface tension, and D the density of the liquid and d that of the vapour. If we multiply both sides by M, the molecular weight, we get $\frac{M}{D-d}\gamma^{\frac{1}{4}}$ = constant ; and this constant, which may be taken to be the molecular volume measured at a standard internal pressure, is called by Sugden the *parachor*.[2] The values of this new constant show the same kind of additive and constitutive relations as those of the uncorrected molecular volume, the value for a molecule being expressible as the sum of a series of terms for the constituent atoms, together with others for particular forms of linkage, such as a double bond or a closed ring ; but the agreement is much closer, and the difficulty of selecting comparable temperatures is removed, since the parachor is independent of the temperature. The following table shows the values for some of the commoner elements, and also for those constitutive influences which have to be taken into account ; these latter are in the first instance confined (apart from a small correction for the ester group) to the effects of unsaturation and ring-closure, which have recently [3] been shown to conform to a simple rule : if N is the number of hydrogen atoms required to convert the substance into a saturated open-chain compound,

[1] Sugden, *J. C. S.* 1924, 125, 1185 : Sugden, Reed and Wilkins, ibid., 1925, 127, 1525 : Sugden and Whittaker, ibid., 1868 : Sugden and Wilkins, ibid., 2517.

[2] It might have been expected that in order to allow for the effect of internal pressure it would be necessary to know the compressibilities as well ; but the agreement between the calculated and observed values of the parachor shows that this provides a valuable means of determining the structure which is independent of a knowledge of the compressibilities.

[3] Sugden, *J. C. S.* 1927.

and Z the number of atoms in the ring (taken as two for double links), then the increase of the parachor for the molecule $= 23{\cdot}2 \times \frac{N}{Z}$.

VALUES OF THE PARACHOR

Elements				*Constitutive terms.*	
H					
17·1					
C	N	O	F	Double link	23·2
4·8	12·5	20·0	25·7	Triple link	46·4
Si	P	S	Cl	3-ring	15·5
12·0	37·7	48·2	54·3	4-ring	11·6
				5-ring	9·3
			Br	6-ring	7·7
			68·0		
			I		
			91·0		

O_2 in esters 60·0 (theory for two oxygen atoms and one double link 63·2).

The theory was tested with some 200 liquids, mainly organic, and the calculated values agreed with the observed usually within 1 per cent., and practically always within 2 per cent.[1] So close an agreement gives one great confidence in the soundness of the method.

When however an extensive series of doubly-linked compounds was examined, it was found that they fell into two classes: whilst a large number (containing the groups C=C, C=O, C=S, N=O) gave results in accordance with the theory, others did not; instead of showing an increase for the double link of 23·2 units (within one or two units out of a total parachor of 100–300), they showed a small decrease, amounting on the average to −1·6. The difference between the two classes is far outside the limits of experimental error, and the distinction is quite sharp; the compound either shows the large rise or the small fall, and never an intermediate value. It is therefore clear that the ' double bonds ' of the traditional formulae represent two different kinds of link. We have already come to the conclusion, on quite different grounds, that this is so: there is the true double link of four shared electrons, and the co-ordinate link (two shared electrons) of type (1) (with a divalent atom like oxygen as acceptor, as in the amine oxides), which, as we have

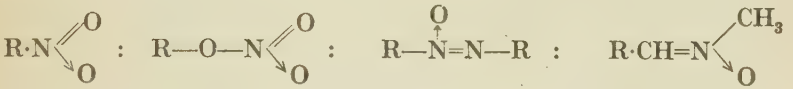
[1] As an example we may take propylene C_3H_6. The calculated value for the parachor is $3 \times 4{\cdot}8 + 6 \times 17{\cdot}1 + 23{\cdot}2$ (for the double bond) = 140·2. The observed value is 139·9.

seen, was also written in the structural formulae as a double bond. The parachor provides us with a means of distinguishing between them. The molecules which give an increase of 23·2 obviously contain true double links (the increase is exactly repeated if the double link is replaced by a triple link), while those which give a fall of 1·6 contain a co-ordinate link : there is no double link to increase the parachor, and the small diminution is presumably due to electrostatic attraction.

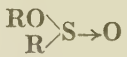
The structures which these measurements indicate are shown in the following list of formulae (R = alkyl or aryl).

$R{\cdot}CH{=}CH{\cdot}R$: $R_2C{=}O$: $(RO)_2C{=}O$: $S{=}C{=}S$
$R{\cdot}N{=}C{=}S$: $R{\cdot}O{-}N{=}O$

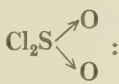
. . . . . .



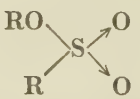
$Cl_2P{\rightarrow}O$: $(RO)_3P{\rightarrow}O$:

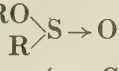


$Cl_2S{\rightarrow}O$:



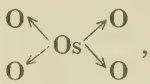
$(RO)_2S{\rightarrow}O$:



Apart from the case of osmium tetroxide, which will be discussed later, these conclusions are very satisfactory, because they entirely confirm the other evidence. All the double links in which one or both the atoms are carbon are shown to be real, with four shared electrons. The contrary suggestion of Lowry, that this link should be written as co-ordinate, is extremely improbable, since it implies at once the reduction of an octet to a sextet, and a disturbance of the electrostatic equilibrium, and also ascribes to the molecules electrical and stereochemical properties which they do not possess. On the other hand, we have proof that the covalency of nitrogen cannot exceed four, so that the NO_2 group in the nitro-compounds and in the nitrates (but not in the nitrites) must have a co-ordinate link. With phosphorus and sulphur, although the covalency can rise above four, there is strong evidence that it does not do so in most of the compounds with oxygen ; and the presence of a co-ordinate link in the sulphinates  is directly confirmed by the stereochemical evidence (see Chapter XIII).

The singular point about Sugden's results is that in every instance they involve the maintenance of the octet. They rule out on the one hand the co-ordinate link for carbon, where it implies the reduction of the octet to a sextet, and on the other the older formulae for the compounds of nitrogen, phosphorus, and sulphur, where these assume a covalency higher than four, and hence an expansion of the valency group beyond eight.

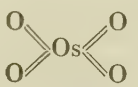
The one compound for which Sugden's conclusions appear to me to be incompatible with the other evidence is osmium tetroxide, because this is the only molecule he has dealt with in which there is reason to suppose a valency group larger than eight. The parachor for osmium tetroxide is 154·0. The value for oxygen is 20·0. If we assume that the osmium has an octet, there must be four co-ordinate links in the molecule



and the value for Os will be :

$$\text{Os} = 154{\cdot}0 - 4 \times 20{\cdot}0 + 4 \times 1{\cdot}6 = 80{\cdot}4.$$

On the other hand, if the molecule is analogous to OsF_8, and has four true double links



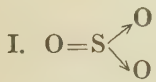
we should have, according to Sugden's values :

$$\text{Os} = 154{\cdot}0 - 80{\cdot}0 - 4 \times 23{\cdot}2 = -18{\cdot}8$$

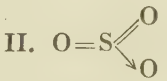
We have no other evidence of the value of the parachor of osmium, but from very rough data for neighbouring elements we should expect to find it between 60 and 100. Hence Sugden concludes that the first formula is correct. The arguments in favour of the eight-covalent structure will be given later : the most obvious are the relation to the octofluoride and the volatility (boiling-point 100°, molecular weight 255). Sugden's argument seems at first sight conclusive, but on examination it will be seen that there is a difficulty. In the first place, the close agreement between theory and observation which he obtains with the other substances cannot be adduced here, for lack of

other data as to the parachor of osmium. Secondly, in all the substances for which the agreement was found to be close, the evidence shows the presence (in every atom except hydrogen) of an octet. We have therefore no proof that his values hold good when the valency group expands ; we should in fact expect that this would affect the molecular volume, and that in addition to the constitutive factors of the parachor already mentioned, another would be needed to allow for the change in size of the valency group. This would presumably be negative : the high stability and screening effect of the octet as compared with any other arrangement of the outer electrons suggest that when there is a larger valency group the external field is stronger, and the attached atoms are more closely held ; just as we find that in zinc, where the group next to the valency electrons is eighteen, the volume is much smaller than in calcium, where it is eight. In osmium tetroxide, if the metal is really eight-covalent, we have an extreme case of this effect, since the valency group has expanded from eight to sixteen ; and we may conclude that if this occurred, it would considerably reduce the parachor, so that the fact that such a formula would give a negative value for the parachor of osmium if no allowance is made for the change in the valency group, is not conclusive evidence that the formula is wrong.[1]

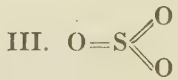
If no more than this could be said, the objection might be thought fanciful. But there is definite evidence in its favour. Sulphur trioxide (in the monomeric form) may have any one of three formulae, which are given below, with the size of the valency group in the sulphur, and the parachor calculated on Sugden's values :



Val. Gp. 8
P = 129·0



Val. Gp. 10
P = 153·4



Val. Gp. 12
P = 177·8

[1] There is no intrinsic improbability in a negative parachor value for a particular atom : what is called the parachor of an atom is really the change in the parachor value for the whole molecule caused by the introduction of that atom, and if it causes the other groups to approach more closely, the total effect may be a contraction, just as an alkaline oxide has a smaller molecular volume (the parachor is of course unknown) than the metal it contains.

The work of Le Blanc and of Smits [1] has shown that sulphur trioxide, even in the low melting α-form, is a mixture of more than one modification, and that the proportions vary with the temperature ; so we should not expect very constant or very concordant values of the parachor, but we should expect, if Sugden's view is right, that they would come between the limits given above, of 129–178. Berthoud [2] has measured the surface tension and the density of sulphur trioxide over a considerable range of temperature, and from his results the following values of the parachor can be calculated :

at 19° P = 100·4
at 44·9° P = 103·4
at 78° P = 106·2

Thus the observed value is lower than that calculated for any of the three possible formulae : indeed it is lower than the sum of Sugden's values for one sulphur and three oxygen atoms (without any allowance for the linkage), which is 108·2. This strongly suggests that an increase in the valency group causes a considerable diminution in the parachor, and that until we know how much allowance should be made for this, we cannot employ the method for the determination of structure except when the observed values agree closely with those calculated on the assumption that the octet is maintained : for it is very improbable that the term representing the change in the valency group would happen exactly to counterbalance in every case that required by the change of linkage.

Sugden's method thus promises to be of great value for the determination of structure ; but it cannot be fully applied until we know the effect of a change in the valency group. This can only be learnt from the examination of substances with atoms of a covalency greater than four. The experimental difficulties are unfortunately great : the preparation of compounds like sulphur hexafluoride or osmium octofluoride and the measurement of their surface tensions are not easy ; but we may hope that these difficulties will soon be overcome.[3]

[1] Le Blanc and Rühle, *Ber. Sächs. Akad. Wiss.* 1922, **74**, 106 : Smits and Schoenmaker, *J. C. S.* 1924, **125**, 2554.

[2] *Helv. Chem. Acta*, 1922, **5**, 513.

[3] Sugden's latest results (*J.C.S.* 1927, 1173) would seem to support these conclusions, although he interprets them differently. He finds the parachors of antimony and phosphorus pentachlorides to be 26 units lower than the

sum of the atomic constants. On the theory we have adopted, the central atoms of these molecules have valency groups of 10, and so a diminution of the parachor is to be expected. Sugden maintains the 'octet rule', that the valency group cannot exceed 8, and hence supposes that in these compounds two of the chlorine atoms are attached by 1-electron links. He points out that the change from a link of four shared electrons (X=O) to a co-ordinate link of two (X→O) with the consequent electrostatic displacement, causes a fall in the parachor of 23·2 + 1·6 = 24·8. He argues that the change from a normal covalency to a 1-electron link might be expected to cause half as great a fall, so that if the pentachlorides contained two 1-electron links in the molecule, the fall should be 24·8, which is very nearly what is observed. The numerical agreement is remarkable, but it is not a sufficient reason for adopting the 'octet rule' in the face of the other evidence, if there is any relation between the structure of a link and its stability. As we have seen, the 1-electron link, in those few molecules in which it is undoubtedly present, is very unstable, while the octet rule would require us to assume the presence of four such links in sulphur hexafluoride, one of the most stable of known compounds.

VIII

MOLECULAR ASSOCIATION

THE term association, especially in connexion with liquids, is familiar, and various properties which it involves are easy to enumerate, but they are more difficult to relate rationally to one another. They become easier to understand when we realize that such substances are essentially co-ordinated compounds, and that their behaviour depends on that fact. It will therefore be convenient to discuss these compounds here, and also to consider the relation of their properties to the general problem of solubility.

It has long been known that liquids tend to fall into two classes, of which water and the hydrocarbons are extreme examples, the members of each class being as a rule more soluble in one another than in a member of the other class. With the development of physical chemistry under the influence of van 't Hoff and Arrhenius, further differences between the two classes became evident. It was shown that liquids of the water class were ionizing solvents, that they had higher dielectric constants (which, as J. J. Thomson and Nernst pointed out, would account for their ionizing power), and that they tended to polymerize both in solution and in the pure liquid state, a tendency obviously related to their abnormally high boiling-points. The two classes therefore became known as associated and non-associated liquids. As more was learnt of the physics of the liquid state, and the theory of corresponding states, it was seen that while the behaviour of non-associated liquids often approximated closely to that of an ' ideal ' liquid, that of associated liquids departed widely from these simple laws,[1] which was indeed to be expected, since in their case the definition of the molecular weight was uncertain and variable. In the same way, while many of the properties of mixtures of non-associated liquids (for example, the specific volume, refractive power, and vapour pressure) are approximately, and sometimes almost exactly, the weighted means [2] of those of their components, this is not even roughly

[1] See Turner, *Molecular Association*, 1915, Chapter V.

[2] If a mixture contains the molecular fraction x of component A, for which the property has the value a, and hence $1-x$ of B, for which it has the value b, the weighted mean value for the mixture is $x.a+(1-x).b$.

true of associated liquids. Hence the two classes are sometimes known as abnormal and normal. The terms ' polar ' and ' non-polar ', which are now often applied to them, should be avoided, as they are ambiguous. They originated in a paper published by G. N. Lewis in 1913,[1] in which he distinguished two forms of chemical combination, differing ' not only in degree but also in kind ', a polar form, as exemplified in potassium chloride, and a non-polar, as in methane. In this paper, which contributed greatly to the recognition of the two forms of atomic linkage, he gives a list of the properties of each class of substances. While his non-polar class practically consists of what we should call non-associated covalent compounds, his polar class includes both salts and associated liquids. As a result of his work the terms polar and non-polar are commonly used of liquids to mean the same as associated and non-associated, or abnormal and normal : while these same terms are also used in a different connexion to denote electrovalent and covalent molecules respectively. This leads to an unfortunate confusion of thought, since associated substances are not necessarily ionized or electrovalent, and in fact, according to later evidence, many of them are not ionized at all. It is true that associated liquids in the pure state usually have a minute conductivity (commonly less than 10^{-7}), but as we now realize that weak electrolytes are weak because they are mainly in the covalent form (indeed Lewis suggests this in the paper in question) this is rather evidence against than for their being ' polar ' in the electrovalent sense. The ambiguity is best avoided by applying the terms polar and non-polar only to the forms of atomic linkage, and calling these two classes of liquids either associated and non-associated, if we are mainly concerned with their polymerization, or abnormal and normal, if we are dealing with their general properties.

Later investigations of the properties of associated as compared with non-associated liquids have furnished an immense number of new facts, but they cannot be said to have cleared up the question as a whole. The truth is that while no one doubts the existence of this distinction, and while the general order of substances is much the same whatever method of investigation is used, passing from an extreme example of association or abnormality like water through the lower and then the higher organic acids and alcohols to the ketones, ethers, and esters, and finally the aromatic and then the paraffin hydrocarbons, the

[1] *J. Amer. Chem. Soc.* **1913, 35, 1448.**

exact order obtained is somewhat different according to the particular property on which it is based. The order of abnormality as determined by any of the usual methods of measuring association agrees with that of the dielectric constants and the ionizing powers on the whole, but not in detail. Even for the degree of association very diverse values are obtained according to the method used for determining it.[1]

The impossibility of finding any general measure of abnormality suggests that we are dealing with a selective action, that is, with chemical affinity: so that one associated solvent, for example, may be more abnormal than another in its action with one solute, and less abnormal with another. In all well-marked examples of associated liquids there is evidently a real combination between the molecules,[2] and as these molecules are in the ordinary sense saturated, this must arise through the formation of co-ordinate links. The great majority of associated substances contain a hydroxyl group; and that the association depends on both the atoms of this group is evident if we compare, say, ethyl alcohol with ethyl ether on the one hand and ethane on the other: in the absence of either the hydrogen or the oxygen of the hydroxyl group the association does not occur. The polymerization must therefore arise through this hydrogen acting as acceptor and the oxygen as donor, which would formally permit of the linking up of an unlimited number of molecules:

$$\begin{matrix} & R & & R & & R & & R & \\ H-O & \rightarrow H-O & \rightarrow H-O & \rightarrow H-O & \rightarrow \end{matrix}, \text{ \&c.}$$

It is not probable that the number so linked exceeds three or four. In water, for example, the structure of ice (presumably the highest polymer) points to three.

There is evidence [3] that associated substances can be divided into two groups. In one, the association factor is limited to two, but this limit is nearly reached (in solution in non-associated solvents) at comparatively low concentrations. To this group

[1] See, for example, the list of values obtained by different methods in Walden's *Molekulargrösse von Elektrolyten*, 1923, p. 58.

[2] This sometimes extends even to the vapour, as with formic and acetic acids; water vapour probably contains from 5 to 10 per cent. of double molecules (Bose, *Z. f. Elektrochem.* 1908, **14**, 269). But it is very difficult to detect a small amount of polymerization in the vapour, as an observed excess of the vapour density over that required by the simple gas laws may be due to the a of the van der Waals equation.

[3] See Auwers, *Z. phys. Chem.* 1899, **30**, 300.

the carboxylic acids belong : formic and acetic acids are largely dimeric even in the vapour at the boiling-point.[1] In the second group, which includes alcohols and phenols, the degree of association is often less than with the first group in dilute solution, but the polymerization can apparently proceed to a much higher limit : [2] the value of this limit cannot be determined, as the laws on which the molecular weight determinations are based no longer hold (see later, p. 149) in more concentrated solutions.

Associated substances have all the characteristic properties of co-ordinated compounds, especially the low volatility and the high dielectric constant. The evidence of the volatility is sometimes misunderstood, and it is said that the abnormally high boiling-points of these substances are explained by their polymerization. But unless this is much greater than we have any reason to suppose, it will not account for the whole effect. For example, the ethers boil about 60° lower than the corresponding thio-ethers. Hydrogen sulphide boils at −61°, and so unimolecular H_2O should boil about −120°. If the real formula of water is H_6O_3 (and it is very improbable that its average polymerization is even as great as this at 100°), its true molecular weight is not 18 but 54. This will account for a rise in the boiling-point, but not for so large a rise as is actually found. Hydrogen selenide (mol. wt. 81·2) boils at −42°, and butane (mol. wt. 58) at +1°. Evidently the polymerized molecules themselves are much less volatile than corresponds to their molecular weights, as we should expect from the presence of the co-ordinate link. The high values of the dielectric constant (water, formamide, and hydrogen peroxide over 80, methyl alcohol 35, ethyl alcohol 27) are further evidence of co-ordination ; the ionization of an associated substance in the pure state is as a rule negligible, and there is no reason why the polymerization

[1] Drucker and Ullmann (*Z. phys. Chem.* 1910, **74**, 604) have shown that the measurements of Ramsay and Young of the density of acetic acid vapour must be corrected for the amount absorbed on the glass surfaces. When allowance is made for this it is found that the vapour (at 80−110°) contains roughly an equal number of single and double molecules. Formic acid appears to behave in the same way. It is doubtful whether ethyl alcohol vapour is associated under these conditions at all.

[2] For examples of this difference see the curves given by Brown and Bury, *J. Phys. Chem.* 1926, **30**, 701. The arguments of these authors against the occurrence of polymerization in associated substances cannot however be regarded as valid.

in itself, if it were not accompanied by the formation of co-ordinate links, should increase the dielectric constant.

Other properties of associated liquids are direct results of the polymerization, such as their departure from the simple general laws deduced from the equation of state ; these laws are colligative—they depend on the number of molecules present—and the size of the molecule of an associated liquid is an uncertain quantity, and is a function of the conditions. The same may be said of their failure to comply with the mixture law. If two liquids A and B, each containing polymerized molecules, are mixed, these polymers will to some extent dissociate, and new complexes, containing both A and B molecules, will be formed, whose production will naturally modify the properties of the mixture. This also accounts for the considerable heat (and volume) effects often observed on mixing such liquids. With non-associated liquids, since there is no combination between the molecules, the components have little influence on one another, and their heats of mixing are usually negligible.

Another characteristic tendency is that of solutes in non-associated liquids to associate, and in associated liquids to dissociate, whether by this we mean the separation of polymerized molecules into their unimolecular constituents, or that of electrolytes into their ions. There are two reasons for this : first that the high dielectric constant of the associated solvent weakens the attraction between the ions ; and secondly that an associated solute will tend to combine with an associated solvent. In dilute solution, with which we are mainly concerned, the complexes so produced will mostly not contain more than one simple molecule of solute apiece : if A is the solute and B the solvent, they will be AB_n. The methods of determining molecular weight in solution really give not the molecular weight of the solute, but the number of molecules produced in solution by a given weight of solute ; they take no account of the weight of solvent combined with these molecules, which only affects the result when the solution is so strong that the amount of solvent thus withdrawn is appreciable. Hence where the actual molecules in solution are AB_n, the observed molecular weight is that of A alone, and the solute is said to be dissociated into simple molecules. If this solute is dissolved in a hydrocarbon, which has no tendency to combine with it, the solute molecules are free to combine with one another. Combination with the solvent no doubt has a considerable effect in promoting the ionization

of weak electrolytes: if the ions (or one of them) can combine with the solvent, the whole equilibrium

$$\text{M–A} \rightleftharpoons [\text{M}]\text{A} \rightleftharpoons [\text{M}]^+ + \text{A}^-$$
$$\uparrow\downarrow$$
$$[\text{M, solvent}]^+$$

will shift in the direction of ionization. The cation in particular is, as we have seen, often a powerful acceptor, and so is peculiarly ready to co-ordinate with a donor, which an associated liquid must always contain.

The consideration of the abnormality of liquids from the point of view of co-ordination brings out a further point, which explains some of the difficulties of the subject. The association, as we have seen, requires that each molecule should contain one atom which can act as a donor, and another which can act as acceptor: it is only when both are present that the substance can polymerize. But there are liquids whose molecules contain only a donor, and others in which there is only an acceptor. Such substances will not polymerize, and in the pure state will behave as normal liquids; but in the presence of a second substance capable of association (and so possessing both kinds of atoms required for co-ordination) they may exert their powers as donors or acceptors, and will then behave abnormally. They thus have properties in common with each of the two main classes of liquids, and their behaviour has been found difficult to explain. Acceptor liquids (if the phrase is permissible) are so unstable, being prone to accept water, and even atmospheric oxygen, usually with decomposition, that comparatively little is known of their physical behaviour in two-component systems: examples are boron trifluoride, stannic chloride, and the zinc alkyls. But donor liquids are quite common, familiar examples being sulphur dioxide, nitrobenzene, and ether, They are not associated, because they have no acceptor, but they readily associate with a solute which has, as all associated solutes have, an acceptor atom. Ether, for example, is a normal liquid as judged by its properties in the pure state, but it is an abnormally good solvent for many hydroxylic compounds, with which it combines like an alcohol, its oxygen co-ordinating with the hydroxylic hydrogen: $(C_2H_5)_2O\rightarrow H–O–R$. Nitrobenzene again, although it is not associated (its high dielectric constant and its low volatility are due to the presence of a co-ordinate link in the simple molecule), behaves as an abnormal solvent with certain associated

solutes, as will be shown in the next section. The peculiar properties of amines, which are also difficult to place in the series of liquids, are probably to be explained by the molecule possessing strong donor and weak acceptor properties, so that its abnormality is slight in the pure substance, but can become strong in presence of a suitable solute.

Solubility

The most practically important difference between these two classes of liquids is in their solvent power. Speaking generally, a liquid is a better solvent for members of its own class than for members of the other, and associated liquids (including donors like sulphur dioxide) are practically alone in being able to dissolve inorganic salts. While all non-associated liquids are infinitely miscible with one another, and all extreme members of the associated class, such as water and the lower alcohols and acids, are also miscible with one another, water will only dissolve to a very limited extent in non-associated liquids: and other pairs of a normal and an abnormal liquid, such as benzene and a lower alcohol, although they do not actually form two liquid layers, can be shown not to be far removed from separation. We have seen that associated molecules, owing to the electrostatic disturbance resulting from the co-ordinate link, must attract one another. An attempt has been made to determine the internal pressure to which this attraction gives rise, and to use it as a measure of the abnormality. Although this has not been much more successful than other attempts to obtain a quantitative value of abnormality, there is no doubt that the attraction exists. If such a liquid is mixed with a normal liquid like hexane, in which the molecules have a very weak external field, and consequently very little attraction for one another, there will be a tendency for the two kinds of molecules to separate, the associated congregating together, and as it were squeezing out the others. If this goes far enough, the liquid will separate into two layers.

We can thus see why these liquids are imperfectly miscible. Usually however when we talk of solubility we are not thinking of the miscibility of liquids, but of the solubility of a solid in a liquid. In order to make it clear how this is affected by the character of the solvent and the solute, the general conditions determining solubility must be briefly reviewed. No more will

be said of them than is necessary for the understanding of the question under discussion.

A saturated solution being one which will dissolve no more solid, it follows that the vapour pressure of the solid at the temperature in question must be equal to the partial pressure of the same substance in the vapour from the solution, for if it were not, the solute would distil either from the solution to the solid or vice versa, and the two phases would not be in equilibrium. The solvent power will therefore be determined (at least in part) by the partial pressure of the solution. Suppose [1] we have a solvent A and a solute B at temperature T. T is obviously below the melting-point of the solute, but we may imagine that the solute can be obtained in a supercooled condition at this temperature, and that in this liquid condition it has a vapour pressure p. If increasing quantities of the solvent A are added to the superfused solute, its partial pressure will fall, reaching zero at the point A, where the solution is infinitely dilute. We shall therefore have (Fig. 3) a curve representing at temperature T the change of the partial pressure of the solute with concentration. This will have one of the three forms given in Fig. 3 : it will either be a straight line (I), or it will lie above this (II : ' positive curve ') or below it (III : ' negative curve '). Now since the temperature is below the melting-point of the solute, the vapour pressure of solid B must be less than p, that of the supercooled liquid : let it be represented by π. A horizontal straight line drawn through π will cut the three curves at three different points, corresponding to the molecular concentrations S_i, S_{ii}, S_{iii}. These are the concentrations at which the partial pressure of B in the vapour from the solution is equal to the vapour pressure of solid B. Hence these must represent saturated solutions ; and S_i, S_{ii}, or S_{iii} will be the solubility (in molecular proportions) of B in A at this temperature, according as the partial pressure curve is I, II, or III. In other words, the amount of solvent in a saturated solution is that required to reduce the vapour pressure of the supercooled liquid solute as much as it is reduced by conversion into the solid form. This diagram is of fundamental importance to the understanding of the factors which determine solubility. They are obviously two : (i) the ratio π/p of the vapour pressure of the solid solute at T to that of the supercooled liquid, and (ii) the shape of the partial pressure curve ; the first depending on the solute alone, and

[1] See Hildebrand, *Solubility*, 1924, p. 35.

the second both on the solute and on the solvent. The first factor π/p is determined by the molecular heat of fusion Q,[1] the temperature of observation T, and the melting-point T_0, according to the equation

$$\log \pi/p = \frac{-Q}{4{\cdot}58} \times \frac{T_0 - T}{T_0 T}.$$

Now Q usually lies between 4 and 7 kilogram-calories per gram-

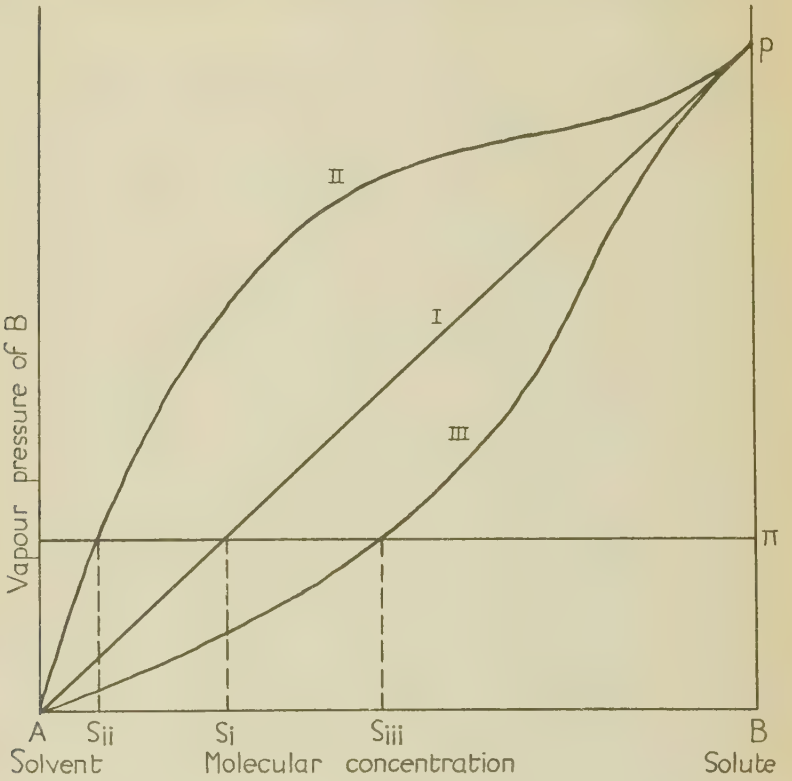


Fig. 3

molecule, and very seldom is outside the limits 2–10 kgr. cals. $T_0 - T$ may vary from 10° or less to 1000° or more. Hence the height of the melting-point has commonly much more effect on

[1] Strictly speaking, this is not constant, but falls slightly with the temperature, the coefficient being equal to the difference between the specific heats of the supercooled liquid and the solid, of which the former is always the greater ; and allowance should be made for this in the equation which follows ; but the error introduced by neglecting it is usually small.

this factor than the heat of fusion ; this is the basis of Carnelley's rule, that of similar substances (that is, where the partial pressure curves are not very different) the one which has the lower melting-point is the more soluble. Two extreme examples may be taken :

(i) For naphthalene at 25° ($Q = 4{\cdot}4$ kgr. cals., $T_0 = 80°$) : $\pi/p = 0{\cdot}31$.

(ii) For sodium chloride at 25° ($Q = 7{\cdot}22$ kgr. cals., $T_0 = 804°$) : $\pi/p = 0{\cdot}000148$ (about 1/7000).

These values are the actual solubilities (in molecular fractions) which the substances would have at 25° in any solvent with which they gave the straight line partial pressure curve (I). With non-associated substances like naphthalene in solvents of the same type, the partial pressure curve very nearly is a straight line, and so the observed solubilities are often very near the calculated : thus that of naphthalene in benzene at 25° is (in molecular fraction) 0·29.

The value of the solubility calculated in this way (from the heat of fusion) for any solvent with which the solute behaves ideally (giving a straight line partial pressure curve) is an important characteristic of the solute, and may be called its ' natural solubility '.[1] The departure of the actual solubility in any solvent from this value is a measure of the departure of the partial pressure curve from a straight line. If the observed solubility is less than the ' natural ', the curve is of type II (positive) : if greater, it is of type III (negative). As examples we may take the solubilities of naphthalene and of sodium chloride in water and benzene, using the values of π/p already obtained for these solutes. The solubility of naphthalene in water is minute, perhaps at the outside 0·1 gram per litre. That of sodium chloride in benzene is smaller still : it is too small to be measured, but we may take it to be of the order of 1 mgr. per litre. The observed and calculated values in grams per kgr.

[1] The following are the values in molecular percentages ($= \pi/p \times 100$) of the ' natural solubilities ' at 25° of substances with heats of fusion of 4 and 7 kgr. cals. per gr.-mol. respectively (the normal limits of variation), according to their melting-points :

M. Pt.	Q = 4 k. cals.	Q = 7 k. cals.
50°	59·3	40·1
100°	25·9	9·42
200°	8·33	1·29
500°	1·58	0·071
1000°	0·57	0·012

of solvent at 25° are as follows (the calculated values in water will depend on what we take as its molecular weight, since this affects the conversion of molecular into weight proportion) :

SOLUBILITIES IN GRMS. PER KGR. OF SOLVENT

Naphthalene :
in benzene : calculated 738 : observed 708 : ratio 0·96
in water : calculated (as H_2O) 3200 / (as H_6O_3) 1100 : observed 0·1 : ratio 0·00003 / ratio 0·0001

Sodium chloride :
in benzene : calculated 0·11 : observed 0·001 : ratio 0·01
in water : calculated (as H_2O) 0·48 / (as H_6O_3) 0·16 : observed 361 : ratio 750 / ratio 2300

The non-associated solute has in benzene nearly its ' natural ' solubility, but in water only a minute fraction ; the ionized solute, whose natural solubility is much smaller, is still less soluble in benzene, but in water it is enormously more soluble than the calculation requires. This shows that the partial pressure curve of naphthalene is nearly a straight line in benzene, and is highly positive in water, while that of sodium chloride is positive in benzene, and highly negative in water.

The next question is what are the causes of the various forms of partial pressure curves. Positive curves (which give unduly low solubilities) can be shown to be given by two components which are approaching the temperature at which they will separate into two layers ; they are therefore due, as has already been explained, to a large difference in the internal pressures of solvent and solute. Straight line curves of course indicate that the molecules are indifferent to one another, which can only happen if both components are of the normal, non-associated type. Negative curves (abnormally high solubility) can only be explained by supposing that some kind of combination occurs between the components. In an extreme case, as with the partial pressure of methylamine in presence of a sulphonic acid, the combination will be complete until an equimolecular mixture is reached : the salt will not be dissociated into its components at all, and up to this point there will be no partial pressure of the amine whatever ; the curve will fall from p, the value for the pure amine, to zero at 50 molecules per cent. (*ps*, Fig. 4). With a weak acid and base (say ammonia and hydrocyanic acid) the salt will be largely dissociated into hydrocyanic acid and ammonia ; there will be a perceptible vapour pressure at 50 per cent., and the curve will be smoothed off, as at x in the

figure. Thus when the solute combines with the solvent, the curve must lie between *ps* and the straight line *p*A, being always negative (the solubility greater than the natural), and approaching the straight line as the combination becomes weaker.

On these principles we can see what will be the general effect on the solubility of the character of the solvent and the solute respectively. We have to consider two kinds of solvent, non-associated and associated, and three kinds of solutes, non-

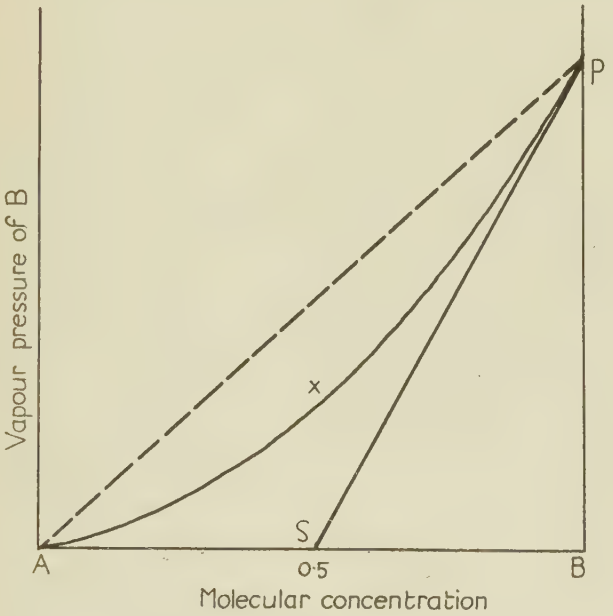


Fig. 4

associated, associated, and ionized ; true liquid salts can only exist at high temperatures (with the possible exception of a few strong acids such as perchloric), and they need not be considered as solvents.

The ' natural ' solubility depends mainly on the melting-point of the solute : if this is high, it will be small, and if low, large ; if the solute is liquid (i. e. at or above its melting-point) the natural solubility is of course infinite. A high melting-point is caused (i) by an attractive force between the molecules and (ii) by a high molecular weight. Hence non-associated substances (with normally covalent molecules) will have low melting-points unless their molecular weights are large. Associated

substances (co-ordinated) will have their melting-points raised by the increase of molecular weight caused by the association, and probably also by the attraction due to the co-ordinate links : but experience shows that neither of these produces a large effect. Ionized substances (those which are still ionized in the solid state) will have high melting-points owing to the large force between the charged ions.

The relation between the natural solubility and that observed in a particular solvent depends on the shape of the vapour pressure curve. With non-associated solutes in non-associated solvents this approximates to a straight line, and the solubilities come near to the natural. With the same solutes in associated solvents, especially in water, the vapour pressure curve is strongly positive, owing to the tendency to separation, and the solubilities are therefore below, and often far below, the natural. Associated (co-ordinated, not materially ionized) solutes in non-associated solvents tend for the same reason to have positive partial pressure curves and an abnormally low solubility : but against this must be set the rise in molecular weight, which increases the weight per cent. dissolved, and also the apparent molecular percentage, if the simple formula weight is taken (as it practically must be) to represent the molecule. In associated solvents their solubilities are increased, owing to their cross-association with the solute. Ionized solutes, on account of their high internal pressure, give highly positive partial pressure curves in non-associated liquids, and so have a solubility much below the natural : and as this last is already small on account of their high melting-points, they are as a rule almost if not quite insoluble in such solvents.[1] In associated liquids they tend to give negative curves, owing both to the effect of the high dielectric constant on the force between the ions and to the tendency of the ions to solvate. Hence their solubilities in these liquids may reach very high values.

' Pure donors ' like sulphur dioxide and ether behave as normal substances in presence of normal, and as associated in presence of associated substances.

These conclusions are of value not only from the point of

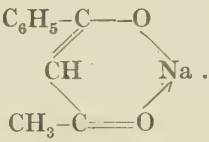
[1] The peculiar solubilities shown in non-associated liquids like chloroform by certain undoubted salts, usually of complex (as ammonium or sulphonium) cations seem to be due to the formation of something like a colloidal solution. The solute molecules are apparently charged, but are highly polymerized. See Walden, *loc. cit.*

view of the general theory, but also because they enable us to infer from the solubility whether a molecule contains co-ordinate or ionized links or neither. If it contains neither, it will show its usually considerable natural solubility in solvents like benzene, and will be much less soluble in water. If it contains co-ordinate links not due to association (like the chelate compounds described on p. 119), and has no donor or acceptor atom, its solubility will as a rule be that of a non-associated substance. The behaviour of associated substances, which usually means those containing hydroxyl groups, is sometimes perplexing. The melting-points may, for reasons not fully understood, be low, and even very low, and hence the natural solubility large: this however is known and can be taken into account. The association tends to make these substances less soluble in hydrocarbons and similar solvents, especially if the associating groups (as hydroxyl) form a large proportion of the molecule, and the internal pressure is high; but if they have a large 'organic' constituent (covalent non-co-ordinated radical), as in the aromatic acids and the higher alcohols, this diminishes the internal pressure, and they may become comparatively insoluble in water; in that case they often dissolve more readily in ether or alcohol than either in water or benzene. Finally, salts are practically insoluble in non-associated liquids, and as a rule far more soluble in water than in any organic solvent, even a lower alcohol, and far more than we should expect from their melting-points.

Some examples may be given of the practical application of these ideas.

(i) Distinction of ionized and covalent links. The sodium derivative of benzoylacetone [1] might either be a salt (I) or a covalent chelate compound (II):

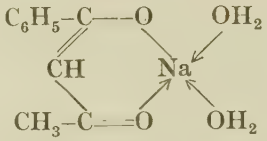
I. $C_6H_5-C(=CH\cdot CO\cdot CH_3)-O\,[Na]$

II. 

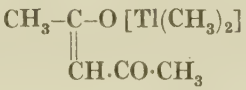
It is found to char on heating without melting, to dissolve readily in water, and to be quite insoluble in benzene and toluene. All these properties are those of a salt, and so we may assume that it has the formula I. If it is recrystallized from aqueous alcohol, it takes up two molecules of water. This might be 'water of

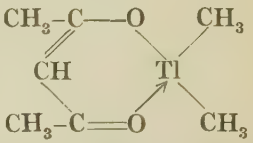
[1] Sidgwick and Brewer, *J. C. S.* 1925, 127, 2379.

crystallization ' in the sense that it was attached to the sodium ion in formula I, giving $[Na, 2H_2O]^+$. If so, the solubility of the hydrated compound should be of the same order as that of the anhydrous salt. But the hydrate is found to dissolve in toluene. This is a clear proof that it is not an ionized but a covalent compound, and its structure must be



A rather less obvious example is that of the acetylacetonate of dimethyl thallium.[1] The iodide of this base $(CH_3)_2TlI$, is an undoubted salt, derived from the strong base $[(CH_3)_2Tl]OH$. Here again, therefore, the diketone compound might either be a salt (I) or a chelate compound (II) :

I. 

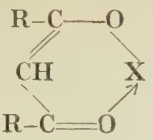
II. 

The compound has a fairly low melting-point, can be sublimed easily in vacuo, and is readily soluble in benzene. All these properties make it clear that the molecule is covalent, and the second formula correct. We should therefore expect that the substance (like beryllium acetonylacetonate) would be slightly if at all soluble in water. It is found however to dissolve readily. Formula II has no associating groups such as hydroxyl to account for this solubility, and the only possible explanation is that the molecule, which alone and in benzene has the structure II, changes in water into the ionized form I. This hypothesis is easily tested. If in water the compound is ionized, then since it is the salt of a strong base and a weak acid, it should be hydrolyzed, and have an alkaline reaction : this it is found to have. Also the solution must contain $[(CH_3)_2Tl]^+$ ions, and therefore give with potassium iodide a precipitate of the slightly soluble iodide of this base ; this also it does.

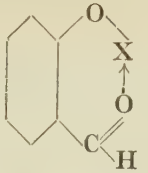
(ii) Distinction between associated and non-associated substances. An example of this is afforded by the case of those compounds (such as the β-diketones, and certain ortho-sub-

[1] Menzies, Sidgwick, Fox, and Cutcliffe, *J. C. S.* 1928, 1288.

stituted phenols, like salicylic aldehyde) which can form chelate derivatives with metals, of such types as



and



There is no doubt that they form ring structures of this type if X is an appropriate metal: the question is whether they do so also when X is hydrogen. This is of importance from its bearing on the maximum covalency of hydrogen. It can be answered by investigating the association of the compounds. If the hydrogen compound is not co-ordinated, it will contain a free hydroxyl group, and hence be an associated substance; if it is co-ordinated, as in the above formulae (X = H), the acceptor properties of the hydroxylic hydrogen are used up, and the substance will be non-associated. Thus the effect of the chelation should be to increase the volatility, and to make the solubility greater in non-associated solvents and less in associated. To find whether this effect is produced, the substance must be compared with analogous compounds. The nearest analogues of the enolized β-diketone derivatives are the isomeric ketonic forms

Enolic Ketonic

These true diketones are in the strict sense non-associated, and behave as fairly normal substances, certainly more so than definitely hydroxylic compounds. Experiment shows that the enolic form is actually more volatile (where this property can be measured) than the isomeric ketone, and that in all cases the ratio of the solubility of the enol to that of the ketone is greatest in the least associated liquids like the hydrocarbons, and less in water and the alcohols. Thus the enols behave even less like associated liquids than the ketones, and cannot have a free hydroxyl group: they must be, at any rate to a very large extent, chelate compounds, with the hydrogen co-ordinated to the second oxygen atom.[1]

In the ortho-substituted phenols [2] we can institute a closer

[1] Sidgwick, *J. C. S.* 1925, 127, 907.

[2] Sidgwick and Ewbank, *J. C. S.* 1921, 119, 979: Sidgwick and Callow, ibid., 1924, 125, 527.

comparison, with the isomeric meta- and para-compounds; these cannot be chelated, because an aromatic derivative cannot form a meta- or para-ring, and so they show how such a molecule behaves when its hydroxyl group is available for association. The results show that whenever the substituent has the necessary structure to form in the ortho-position a chelate six-ring through the hydroxyl hydrogen as with

$$-C\begin{matrix}H\\O\end{matrix}, \qquad -C\begin{matrix}OR\\O\end{matrix}, \quad \text{or} \quad -N\begin{matrix}O\\O\end{matrix},$$

the ortho isomers differ markedly from the meta and para, and always in the direction of being less associated; they are more volatile, and are more soluble in benzene [1] and less in water. The evidence for co-ordination of the hydrogen is conclusive. There is another remarkable point about these phenols, bearing on the general question of association. Auwers [2] has examined the effect of such groups as NO_2 and CHO on the cryoscopic properties of the phenols. The determination of the molecular weight of a phenol by the depression of the freezing-point of a non-associated solvent like benzene gives the usual indication of the association of a solute, that the molecular weight rises rapidly with increasing concentration. Auwers finds that an active group like NO_2 or CHO can produce three different effects. If introduced into the solute (phenol) in the ortho-position it makes it less associated: the rise of molecular weight with concentration becomes less or nothing. In the meta- or para-position in the solute it increases the association. Finally, if it is introduced into the solvent (for example benzene) it makes an associated solute appear less associated: the molecular weight as measured cryoscopically rises less with concentration in nitrobenzene than in benzene. The order of efficiency of different substituting groups is the same for all these three phenomena. These facts are all in accordance with the views which we have

[1] In water the system generally forms two layers, and the critical solution temperature is then a direct measure of the solubility. In benzene this seldom happens, and the solid-liquid curves obtained are of course determined by the π/p values, which largely depend on the melting-points, and are not the same for different isomers. This difficulty can be overcome by calculating from the solubility curves the apparent heat of solution at various concentrations. If the partial pressure curve approaches a straight line, this value will be nearly constant: if it is a positive curve (indicating in benzene that the phenol behaves as an associated substance) the heat values will rise to a maximum (see Sidgwick and Ewbank, *loc. cit.*).

[2] *Z. phys. Chem.* 1903, **42**, 513.

adopted. Phenol itself is associated in benzene, through the oxygen of the hydroxyl as donor and the hydrogen as acceptor:

$$\begin{array}{llll} & C_6H_5 & C_6H_5 & C_6H_5 \\ & | & | & | \\ H—O\rightarrow & H—O\rightarrow & H—O\rightarrow & \end{array}, \text{ \&c.}$$

An ' active ' group is one which contains an active donor, like the oxygen in NO_2 and CHO. In the ortho-position in the phenol this, as we have seen, forms a chelate ring with the hydroxyl hydrogen of the same molecule, and hence prevents association with other molecules, since the hydrogen has acquired its maximum covalency. In the meta- or para-position in the phenol the active group is still able to form a co-ordinate link, but it cannot do so with the hydroxyl hydrogen of the same molecule, since this would involve the formation of a second ring attached to the benzene nucleus in the meta- or para-position, which (no doubt for steric reasons) is impossible. But it is able to co-ordinate with the hydrogen of the hydroxyl group in another molecule, and does so more readily than a hydroxylic oxygen atom : hence the meta- and para-compounds are more associated than phenol itself. If we introduce the active donor group into the solvent (benzene) instead of the solute, we make the solvent able to co-ordinate with the solute, if that is a phenol or other hydroxylic compound,

$$C_6H_5–N\begin{matrix}\nearrow O\rightarrow H–O–C_6H_5 \\ \searrow O\end{matrix}.$$

It will therefore tend (being in large excess) to break up the phenol aggregates : the number of solute molecules will increase, and the ' molecular weight ', as determined cryoscopically, will diminish.

There are one or two further points about associated liquids which should be mentioned. The cryoscopic evidence of association—the fact that the freezing-point of a solvent is less depressed by a solute than its formula weight requires—must be interpreted with caution. This effect is always found when the partial pressure curve is positive, and with a system of associated + non-associated substance (for example, benzene + para-nitrophenol) it is found at both ends of the freezing-point curve—for a dilute solution of benzene in the nitrophenol as well as for the reverse case—since the partial pressure curves of both components are positive. It cannot be supposed that the benzene is actually associated in this solvent, and the freezing-point results obviously mean only that the system is approaching the

condition of separation into two layers. It is true that this implies that one component is associated, and in that sense we may say that the cryoscopic method truly indicates association, but it is not necessarily association of the component whose molecular weight is being determined. For the same reason where polymerization undoubtedly occurs, the absolute values of the association factor which the cryoscopic method gives cannot be accepted as true except where they are reasonably constant over a range of concentrations. The apparent molecular weight of methyl alcohol in benzene solution as calculated from the depression of the freezing-point rises to some thirty times that of the simple formula : this does not mean that thirty CH_3OH molecules actually combine to one, but only that the partial pressure curve is highly positive. With associated solutes of the carboxylic acid class, where the apparent molecular weight rises rather rapidly to twice the simple value, and does not further increase, the results can no doubt be accepted as true.

Another point which should be noticed is the remarkable difference in solvent properties between the aromatic hydrocarbons and the paraffins. One is inclined to regard both groups as representing the extreme of non-association or normality, but in fact there is almost as much difference between them as between benzene and alcohol. The paraffins have an extraordinarily small solvent power, especially for those somewhat associated substances which, owing to a large ' organic ' constituent, are readily soluble in benzene : they are only slightly miscible (even above the melting-point of the solute) with many (not ortho) aromatic hydroxy-acids, with all three nitrobenzoic acids, and even with aniline. Again, while they are miscible with the lower alcohols, a very small trace of water causes separation into two layers, whereas with benzene and alcohol much more can be added : for example, ethyl alcohol containing 10 per cent. of water will dissolve four times its weight of benzene, but only a third of its weight of hexane. Naphthenes (cyclohexane derivatives) are intermediate in this respect between the aromatic hydrocarbons and the paraffins. The reasons for these differences are not known : they are presumably due to the external field of the molecules (and hence the internal pressure) being much weaker with the paraffins ; but the difference in dielectric constant is not large (about 1·8 for the paraffins and 2·3 for the aromatic hydrocarbons), and scarcely seems enough to account for the contrast. It is possible

that the formation of a positive vapour pressure curve depends not on the difference of the internal pressures or dielectric constants of the components, but on their ratio.

There is one class of liquids which has not been mentioned, namely liquid metals. They consist of positive (not necessarily monatomic) ions and electrons. No question arises as to their solubility (in the ordinary sense of the term) in non-metallic solvents : they can only dissolve as ions, and the electrostatic forces so produced prevent the process from proceeding beyond the surface layer unless they are relieved by chemical changes taking place. Solution of a metal in the sense in which we have been using the term can only take place in another metal. Such solutions are outside the sphere of our discussion. It may however be pointed out that separation into two liquid layers is not uncommon among metals (especially alkali metals), probably on account of the high internal pressures which prevail in them.

IX

COVALENCY MAXIMA

CHEMICAL combination consists, as we have seen, in the redistribution of the electrons among the atoms forming a molecule so as to produce more stable groupings, this being effected in three ways—by the formation either of electrovalencies or of normal or co-ordinate covalencies. We have considered the mechanism of each of these forms of linkage, with the properties to which it gives rise, and the means by which its presence can be detected. We have now to consider the electronic groupings so produced: to inquire what groupings are experimentally found to be stable, and how these can be related to the structure of the atom.

We may take first the limits to the size of the valency group. We know that an atom can increase its covalency even after all its own valency electrons are used up, by forming co-ordinate links as an acceptor, and that a valency group of sixteen—a covalency of eight—is possible for some atoms, as for osmium in the octofluoride OsF_8. If so large a group can be formed by atoms in general, it would seem that the possibilities of chemical combination are extraordinarily wide. There is however evidence that this is not so, and that the size of the valency group, or the number of covalencies which an atom can form, is subject to limits which vary with its position in the periodic table. These limits, which could not have been deduced from our present knowledge of atomic structure, but are founded solely on the chemical evidence, may be stated first, and the evidence then discussed.

It appears [1] that the maximum covalency of an atom is:

(i) For hydrogen **2** (4 shared electrons).

(ii) For the elements of the first short period of the table (from lithium 3 to fluorine 9), **4** (8 shared electrons).

(iii) For those of the second short period (sodium 11 to chlorine 17) and the first long period (potassium 19 to bromine 35) **6** (12 shared electrons).

(iv) For the heavier elements (rubidium 37 to uranium 92) **8** (16 shared electrons).

There are faint indications of the possibility of a covalency of 10 in certain elements after the end of the second long period,

[1] Sidgwick, *Trans. Faraday Soc.* 1923, 19, 469: Sidgwick and Callow, *J. C. S.* 1924, 125, 532.

but they are not conclusive. It will be seen that this division cuts across that of the ordinary group valencies, and depends not on the group to which an element belongs, but on its period.

The evidence for this rule is as follows :

(i) With hydrogen we have already seen that there are many reasons for believing that by co-ordination it can acquire a covalency of two : to take only the more conspicuous instances, this must be assumed to explain the structure of hydrofluoric acid and of ice, the association of hydroxylic compounds in general, and the chelate structure of the enolic forms of β-diketones and various ortho-substituted phenols. A higher covalency than two for hydrogen has never been seriously suggested.

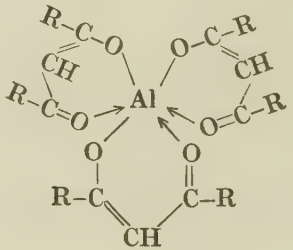
(ii) Of the elements in the first short period (Li –F) all except fluorine [1] have been obtained in a four-covalent form : for example, lithium benzoyl acetone with two molecules of water, analogous to the sodium compound whose formula is given on p. 146 : beryllium acetylacetonate BeA_2 : boron in $Cl_3B{\leftarrow}NH_3$: innumerable compounds of carbon and of nitrogen : and oxygen in the ' basic ' beryllium acetate $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$, a purely covalent compound, in which the unique oxygen atom can be shown to be attached to all four beryllium atoms. That the covalency of these elements cannot exceed four was maintained by Werner,[2] and is supported by a great mass of evidence. We may take first that relating to carbon and nitrogen, the elements of which we know most. Among the enormous number of known compounds of carbon there are none which involve a higher covalency for the carbon than four. Attempts have been made to induce carbon tetrafluoride to form addition compounds of the type so readily given by silicon tetrafluoride (for example, in the fluosilicates) but they have all failed. For nitrogen also the negative evidence is very extensive ; it is supported by Sugden's proof of the co-ordinated structure of the nitro-compounds and alkyl nitrates, and particularly strongly by the behaviour of the

[1] That fluorine should be especially reluctant to assume a high covalency follows from the theory of Fajans. It forms a negative ion of small charge and small size. Both of these properties make the conversion of the electrovalency into a covalency difficult, and we have already seen that fluorine ionizes in positions in which chlorine and the other halogens do not, as in aluminium and stannic fluorides. A covalency of more than 1 is almost unknown for fluorine, and is perhaps limited to the higher polymers of hydrofluoric acid, such as H_3F_3, which presumably must be written $H[F{\rightarrow}H{-}F{\rightarrow}H{-}F]$.

[2] Werner of course called it the co-ordination number.

recently discovered group of compounds in which nitrogen has been made to combine with five hydrocarbon radicals, as in the triphenylmethyl and benzyl compounds of tetramethyl-ammonium $(C_6H_5)_3C[N(CH_3)_4]$ and $C_6H_5CH_2[N(CH_3)_4]$.[1] These compounds have all the characteristics of salts : they are bright red, which for a purely covalent compound of this composition is inexplicable, they are instantly decomposed by water to give the aromatic hydrocarbon and tetramethyl-ammonium hydroxide, and they form conducting solutions in pyridine. The incapacity of the nitrogen atom to form more than four-covalent links is so complete that it overcomes the reluctance of the carbon to ionize, and the products exhibit the colour and the extreme unsaturation (they can only be prepared in the entire absence of air and water) characteristic of the small class of compounds of ionized carbon. It is only when one of the five hydrocarbon radicals is (like triphenylmethyl and benzyl) of the rare type for which ionization is possible [2] that compounds of this kind can be formed at all; attempts to attach five methyl groups to a nitrogen atom invariably failed, since the methyl group cannot ionize.[3]

For boron we have the evidence of its compounds with β-diketones like acetylacetone. As we have seen (p. 120), these diketones form two links with the central atom, one normal and the other co-ordinate, and usually an atom combines with as many of them as it has valencies, forming twice that number of covalencies. Thus aluminium forms a compound

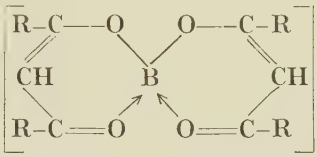


[1] Schlenck and Holtz, *Ber.* 1916, **49**, 603 : 1917, **50**, 274, 276.

[2] Schlenck and Holtz (*Ber.* 1917, **50**, 262) have shown that while the alkyl and phenyl compounds of the alkali metals, such as $NaCH_3$ and NaC_6H_5, are colourless substances insoluble in ether, the benzyl compounds, like those of triphenylmethyl, are bright red, and give conducting solutions in ether. It is clear from the colour and the conductivity that the latter are salts containing ionized carbon, e. g. $Na[CH_2{\cdot}C_6H_5]$, while the former are covalent.

[3] See also Staudinger and Meyer, *Helv. Chem. Acta*, 1919, **2**, 608.

in which it is 6-covalent. We should expect boron, as it is likewise trivalent, to form a similar six-covalent compound BA_3 (A being the univalent chelate radical). But it does not: it reacts with only two diketone molecules, thus becoming four-covalent, and gaining six more electrons (one from each of the two normal covalencies, and two from each of the two co-ordinate links). This gives it nine valency electrons, one of which is expelled, the complex forming a cation



X.

It is difficult to see what reason there can be for this difference in behaviour between boron and aluminium, both of which have the same number of valency electrons, except that the covalency of boron is limited to four, while that of aluminium can rise to six.

With lithium, beryllium, and oxygen the evidence is only negative, but it is fairly convincing. Beryllium, for example, in its salts very readily takes up four molecules of water of crystallization (as does lithium), but not more, forming the stable hydrated ion $[Be, 4H_2O]^{++}$, whereas magnesium in the same salts forms the almost equally stable hydrated ion $[Mg, 6H_2O]^{++}$.

(iii) In the next short period (sodium 11 to chlorine 17) we have plenty of evidence for covalencies of 6, but none for higher values. A covalency of 6 has been established for sodium,[1] and almost certainly (from the hydrated ion) for magnesium. For aluminium we have the acetylacetonate, for silicon the fluosilicates, and for sulphur the hexafluoride. The behaviour of this last compound, as we shall see later (p. 158), shows that sulphur cannot exceed the covalency of 6. The same is shown for silicon by the formula of the acetylacetonate, exactly as the limit of 4 was established for boron: the silicon compound, instead of being SiA_4, which would involve a covalency of 8, is $[SiA_3]X$; as compounds of the type MA_4 are possible with heavier elements of the same periodic group (for example, with zirconium, cerium, and thorium), this must mean that the covalency of silicon is limited to 6.

[1] Sidgwick and Brewer, *J. C. S.* 1925, 127, 2379. In the corresponding lithium compound the metal is only 4-covalent.

In the first long period (potassium 19 to bromine 35) there is abundant evidence that covalencies of 6 can occur. That higher covalencies are impossible is shown (apart from the negative evidence) again by the acetylacetonates. Titanium and germanium, like silicon, form $[TiA_3]X$ and $[GeA_3]X$. Still stronger evidence is the behaviour of selenium hexafluoride, the stability of which to water proves (see p. 158) that the covalency of the selenium is a maximum. We may therefore conclude that up to the end of the first long period the highest possible covalency is 6.

(iv) When we come to consider covalencies of 8, it must be remembered that they cannot be expected to arise, even with atoms which are capable of exhibiting them, except under unusually favourable conditions. It is only the atoms with 8 valency electrons (ruthenium and osmium : iron is excluded as belonging to the first long period) that can form 8 covalencies directly and without co-ordination, as the elements of the sulphur group form 6. In the earlier groups this involves the borrowing of a considerable number of electrons, which causes instability. We might however expect to find 8-covalent atoms in the chelate compounds of the elements of the fourth group, since in these compounds, as we have seen, the covalency is commonly twice the group valency. Accordingly we find that the lightest element which is known with certainty to assume a covalency of 8 is zirconium. While titanium, like silicon, forms a salt $[TiA_3]X$, zirconium forms a neutral compound ZrA_4. Tin also gives chelate compounds in which it is 8-covalent, though not very readily. The only known un-co-ordinated 8-covalent compound of the type MX_8 is osmium octofluoride. But double salts with complex anions of this type, like $Na_3[TaF_8]$, are numerous among the heavier elements : they are formed by zirconium, niobium, molybdenum, tin, cerium, tantalum, tungsten, thallium, lead, thorium, and uranium. There are no certain instances of such anions being formed by elements lighter than rubidium.

These conclusions are supported by other lines of evidence. One of them is the behaviour of the simple halides of the elements with water.[1] If a halide, which may be represented by the symbol $-XCl$, is treated with water, one of four things may happen.

(1) It may ionize :

$$-XCl \longrightarrow -X^+ + Cl^-$$

as with lithium, beryllium, sodium, magnesium, aluminium, &c.

[1] Sidgwick, *J. C. S.* 1924, 125, 2672.

(2) It may hydrolyze (more or less completely) into the hydroxide and hydrochloric acid :

$$-XCl + H_2O \longrightarrow -X-OH + HCl$$

as with the chlorides of boron, silicon, phosphorus, sulphur, &c.

(3) No reaction may take place, as with carbon tetrachloride and sulphur hexafluoride.

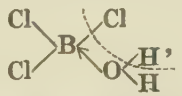
(4) It may hydrolyze in another way, not replacing the halogen by hydroxyl but by hydrogen, with the formation of hypochlorous acid :

$$-XCl + H_2O \longrightarrow -X-H + HOCl.$$

This occurs with nitrogen chloride (and the organic substituted nitrogen chlorides) and with chlorine monoxide OCl_2.

(1) The limitation of this first process, that of ionization, has already been discussed in the light of Fajans' theory. The electrovalency will tend to pass into a covalency as the positive charge on the ion increases, but will do so less readily as the ion grows larger. Hence it is only in the earlier periodic groups that ionization of the halides occurs, and it extends to more highly charged ions as we reach the later periods.

(2) When ionization does not occur, we have the possibility of the water attaching itself to the molecule and reacting with the halogen. Now water is active both as donor and as acceptor : an atom which can increase its valency group can co-ordinate with the oxygen $X \leftarrow O\langle^{H}_{H}$, and one which is able to lend a pair of electrons with the hydrogen $X \rightarrow H-O-H$. In boron trichloride, for example, the boron has a sextet, and so is a ready acceptor : it forms a link with the oxygen, giving

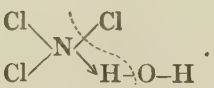


and a chlorine atom is then eliminated with a hydrogen from the water, leaving a hydroxyl group attached to the boron : by a repetition of this process the chloride is hydrolyzed to boric acid. The same happens with silicon tetrachloride, because although the octet of the silicon is complete, it can expand to twelve. It happens also with phosphorus trichloride and pentachloride, and with most the halides of the heavier elements when they do not ionize.

(3) The position of carbon tetrachloride is different. The octet of the carbon is not only complete, but (unlike that of the

silicon in silicon tetrachloride) is incapable of further expansion. The carbon is neither an acceptor nor a donor : it cannot in any way attach itself to the water. Hence no reaction occurs at all : the indifference of carbon tetrachloride even to strong alkali is well known, and the halogens in substituted hydrocarbons are scarcely attacked by water. To find similar inactivity where the covalency limit is six, we must go to the hexahalides of the sixth group, such as sulphur hexafluoride. Here again we have a completely shared valency group of the maximum size, and no reaction occurs. The inactivity of sulphur hexafluoride is its most marked characteristic : it is not attacked even by fused sodium. Selenium hexafluoride is equally inactive, and this is strong evidence that a covalency of eight does not begin until after selenium. On the other hand, tellurium hexafluoride, although in the pure state (for example, in its volatility and stability to heat) it closely resembles the hexafluorides of sulphur and selenium, differs sharply from them in being at once hydrolyzed by water, giving telluric acid. This shows that the valency group is not of the maximum size, and that in tellurium (second long period) a covalency of eight is possible. The other hexahalides of this and later periods—MoF_6, WF_6, WCl_6, UF_6—are likewise hydrolyzed by water. It is remarkable that the same is true of osmium octofluoride, which is perhaps an indication that a covalency of ten is possible for osmium.

(4) Nitrogen chloride (and also chlorine monoxide) is in a different position again. The octet of the nitrogen is complete and cannot expand, but it is not wholly shared. It has a lone pair of electrons, and so can co-ordinate as a donor with the water, giving



The nitrogen having attached itself to the hydrogen of the water remains combined with it, while the hydroxyl comes away with a chlorine atom as hypochlorous acid.[1] Chlorine monoxide hydrolyses in the same way to two molecules of hypochlorous acid : it thus fits in with the scheme, though it cannot be said to lend it much support, as it is difficult to see how the reaction could go any other way.

[1] This explanation of the very peculiar hydrolysis of chlorine covalently attached to nitrogen seems more probable than the hypothesis that such compounds contain a new kind of ' positive ' chlorine.

It is thus possible to account, on the basis of this limitation of the maximum covalency, for all the methods of reaction, or non-reaction, of the simple halides in presence of water.

Many other peculiarities of the periodic table can be explained in the same way. It has been pointed out by G. N. Lewis and others that many elements in the second short period differ markedly from the corresponding members of the first period in their strong tendency to polymerize. This is obvious if we contrast carbon dioxide and carbonic acid with silicon dioxide and silicic acid, or N_2 and O_2 with P_4 and S_8. Lewis explains this by the assumption that the formation of double bonds is possible (or at any rate easy) only for elements in the first period. But apart from these facts there is no reason for making such an assumption, and there are many compounds of the heavier elements whose properties are not easily explicable unless we assume the presence in them of double bonds. A more probable explanation is the difference in the covalency maximum. The carbon in carbon dioxide has fully satisfied both its valency and its covalency : its octet is complete and incapable of expansion. But an atom from the second period which has completed its octet (like the silicon in SiO_2) still has the power of forming two more covalencies by co-ordination, and hence the molecule can polymerize.

Another example is the contrast in stability between chains of carbon atoms and chains of silicon atoms. Saturated hydrocarbon chains, as $-CH_2-CH_2-$, are of course unattacked by water either alone or in presence of acid or alkali. But their silicon analogues react quantitatively to give the silicoethers and hydrogen :

$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- + H_2O \;=\; -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2.$$

a reaction which has been used by Kipping to estimate the number of Si –Si links in the molecule of a compound. This is clearly due to the power of silicon (but not carbon) to act as an acceptor by increasing its valency group :

$$\begin{matrix} SiR_3 \\ SiR_3 \end{matrix} \rightarrow \begin{matrix} H\diagdown \\ H\diagup \end{matrix}O\rightarrow SiR_3 \Big| \begin{matrix} H\diagdown \\ H\diagup \end{matrix}O\rightarrow SiR_3 \rightarrow H_2 + \begin{matrix} HO-SiR_3 \\ HO-SiR_3 \end{matrix} \rightarrow H_2O + O\begin{matrix} \diagup SiR_3 \\ \diagdown SiR_3 \end{matrix}$$

It is particularly to be noticed that this reaction is very highly catalysed by alkalis, that is, by hydroxyl ion. This ion, being negatively charged, will be a very active donor, and will readily

attach itself to the co-ordinately unsaturated silicon, giving the ion $\left[\text{H–O}\rightarrow\overset{|}{\underset{|}{\text{Si}}}\!<\right]^-$; this is the anion of an excessively weak acid $\left[\text{H–O}\rightarrow\overset{|}{\underset{|}{\text{Si}}}\!<\right]\text{H}$, which by co-ordination with its own hydrogen ion passes into the neutral form $\begin{matrix}\text{H}\\\text{H}\end{matrix}\!>\!\text{O}\rightarrow\overset{|}{\underset{|}{\text{Si}}}\!<$, and thus the hydration is effected.

Another example is afforded by the volatile tetroxides MO_4. These are no doubt eight-covalent, with a double link to each oxygen : the alternative formula, with co-ordinate links, would presumably be that of a less volatile compound. This requires that the central atom should have eight valency electrons, a condition fulfilled by iron, ruthenium, and osmium. Of these the last two form remarkably volatile tetroxides, but iron forms none. This must be because the covalency of iron cannot rise to eight, whereas that of the other two metals can.

Many other individual cases might be quoted in support of the rule, some of which will be mentioned in other connexions later : but enough has been said to show that the evidence is strong.

It should be noticed that there are a certain number of compounds which appear to indicate values of the covalency in excess of those allowed by the rule. In none of these have the structure and molecular weight been definitely ascertained. Nearly all of them are either highly complex salts, or compounds containing large numbers of molecules of water or ammonia. These latter will be discussed more fully when we come to deal with the question of solvation (Chapter XI), but it may be said here that they can be interpreted in three ways. (1) They may be crystalline aggregates of independent molecules, their stoichiometric proportions being due to the regularity of the crystalline structure : (2) the water and ammonia compounds may contain double molecules of these associated substances, such as certainly occur in liquid water, so that the number of covalencies of the central atom required for the solvation is only half the number of solvent molecules : (3) they may be real exceptions to the covalency rule. The most probable view would seem to be that adopted by Werner, that they are partly due to (1) and partly to (2). If they are real exceptions to the rule we can only say that the rule expresses the behaviour of the enormous majority of compounds, and that exceptions are rare and apparently erratic.

It must be clearly understood that the rule only states the maximum number of covalencies which an atom can form under the most favourable conditions. The actual value—even the highest value which a given element attains in any of its known compounds—may and often does fall below this. It depends on the nature of the element in question, and on that of the groups with which it is combined. Fluorine, for example, probably owing to its small size, readily forms compounds exhibiting the maximum covalency of other elements, as in $[HF_2]^-$, SF_6, and OsF_8. Chlorine is much less effective: no octochloride is known, and only one hexachloride (WCl_6). Again, if we consider the effect of the nature of the central atom, we find that in both the extreme groups I and VII, especially in I, the highest values seldom appear. With the alkali metals 4 is rare, and 6 is only known in two similar compounds of sodium and potassium. In Group II B (Cu –Ag –Au) the maxima are 6, 6, and 8; but 4 is seldom exceeded. It is obvious that the accumulation of borrowed electrons which a univalent metal needs for a high covalency will rarely be stable. The halogens again give uniformly low values. Fluorine (maximum 4) seldom exceeds 1 and never 2: chlorine and bromine (maximum 6) seldom reach and never exceed 4: iodine (maximum 8), though it shows a markedly greater preference than the other halogens for the higher covalencies, never rises beyond 6.

We have so far considered only the even covalencies. Odd covalencies are of course frequent, although less so than even; but there is no indication of any limit in the periodic table to the odd as there is to the even: there is no sign that, for example, the earlier atoms of the second short period, which can exceed 4, can rise to 5 but not to 6. The relation of an odd value to the next higher even value is that of unsaturation; 1- and 3-covalent atoms are of course familiar, as in H_2 and NH_3; but even here there is a great increase of stability as we go from 3 to 4, as may be seen by comparing the ease with which ammonia forms ammonium compounds with the much smaller tendency of oxygen to form oxonium salts. A covalency of 5, though far less common than either 4 or 6, is well established in the fifth group, where normal 5-covalent compounds can be formed directly: thus we have the volatile compounds PF_5 (B. Pt. −75°, stable up to high temperatures), AsF_5 (B. Pt. −53°), $SbCl_5$ (B. Pt. 140°), NbF_5 (B. Pt. 220°), $NbCl_5$ (B. Pt. 240°), TaF_5 (B. Pt. 229°), and $TaCl_5$ (B. Pt. 242°), to which may

be added IF_5 (B. Pt. 97°); the electrical conductivities of the three chlorides are no greater than that of conductivity water.[1] Covalencies of 7 are very rare, but probably occur in such compounds as $K_4[RuCl_7]$ and $K_2[TaF_7]$.

The relation between the covalency maximum and the structure of the atom, about which something, but not very much, can be said, will be dealt with in the next chapter, after we have considered the method of calculating the valency groups.

[1] Holroyd (*Chem. and Ind.* 1923, 348 : Holroyd, Chadwick, and Mitchell, *J. C. S.* 1925, 2492) found that phosphorus pentachloride had a small conductivity in nitrobenzene solution, although it had none in benzene or ethylene dibromide ; he infers the presence of an ionized form $[PCl_4]Cl$. It is possible that in a donor solvent of fairly high dielectric capacity like nitrobenzene ionization may occur to a small extent, but the work is of a preliminary nature and needs confirmation. In the pure state there is no reason to doubt that phosphorus pentachloride is covalent, like the pentafluoride.

X

STABLE VALENCY GROUPS

THE relation between the nature of a valency group and its stability, and the connexion of this with the structure of the atom as a whole, form the most fundamental problem in the theory of valency, because it is on this stability that the chemical properties of every element depend.

So long as we are concerned only with the isolated atoms in which none of the electrons are shared—either the neutral 'normal' atom, or a monatomic ion—the problem can be dealt with on the lines which Bohr has laid down. The fundamental principles have been established, and the completion of the details may be left to the physicist. But with atoms which are united by shared electrons, forming non-polar links or covalencies—and these are the most interesting to the chemist—the Bohr theory is at present quite unable to deal. We know that the shared electrons enter in some way into the constitution of both the atoms concerned, but we cannot calculate their orbits, or the relations of these to the orbits of the unshared electrons. The mathematical difficulties of this problem are so great that it is unlikely that the physicist will be able to make any great progress with it, unless the chemists to some extent prepare the ground, and by examining the great mass of chemical evidence which they have collected, discover empirically so far as they can what arrangements of shared and unshared electrons do actually occur in stable molecules.

The first step is to determine how many electrons surround the nucleus of an atom in a molecule of known structure, and how many of these are shared with other atoms. As the number in a neutral isolated atom is the atomic number, that in the combined atom (which will obviously vary with the state of combination) may be called the Effective Atomic Number (E.A.N.). The simple rules for determining this may be repeated. We have to find how the original atomic number of the atom in question is modified by the state of combination. We must therefore make the following changes in it.

(1) For every covalency, due to the attachment of a univalent radical, we add 1.

(2) For every co-ordinate valency, such as is formed by

attaching to the atom a complete molecule, when the atom acts as acceptor we add 2 : when it acts as donor, no change is made.

(3) If the resulting complex is an ion, we add the value of its negative or subtract that of its positive electrovalency.

These are the only rules. The following examples will make their application clear.

B in $K[BF_4]$	$5+4+1$	=	10_4
C in CH_4	$6+4$	=	10_4
N in NH_3	$7+3$	=	10_3
N in $[NH_4]Cl$	$7+4-1$	=	10_4
Cl in $H\left[\begin{matrix}O\\O\end{matrix}\!\!\searrow\!\!\swarrow\!\!\begin{matrix}Cl\\Cl\end{matrix}\!\!\swarrow\!\!\searrow\!\!\begin{matrix}O\\O\end{matrix}\right]$	$17+1$	=	18_4
Co in $K[Co(NH_3)_2Cl_4]$	$27+2\times2+4+1$	=	36_6
Co in $[Co(NH_3)_5Cl]Cl_2$	$27+2\times5+1-2$	=	36_6

The subscript number following the E.A.N. gives the number of covalent links formed by the atom. This being the number of pairs of shared electrons, the number of unshared is the E.A.N. minus twice the covalency : e. g. for 36_6 it is $36-2\times6=24$.[1]

Some convention must be adopted to distinguish the shared from the unshared electrons. This may be done by underlining the former (8), but as they always occur in pairs,[2] it is convenient to write them as two equal numbers (4, 4), as if they formed two equal subgroups.[3] It must however be clearly understood that no assumptions are made as to the quantum numbers of the shared orbits (see the discussion on this point, p. 100).

In this way we reach a complete determination of the numeri-

[1] In practice it will be found convenient in examining the compounds of a particular element to count up the ' effective valency ' or ' electronic increment ', which is the total change which must be made in the atomic number to give the E.A.N. (for the two cobaltammines above this is 9_6) ; this can be arrived at by inspection, and is the same for all compounds of the same type ; the E.A.N. is then got by adding the atomic number of the element.

[2] The rare instances in which hydrogen atoms are attached by 1-electron links (see p. 102) must be dealt with separately.

[3] The groups, subgroups, and grouplets of the unshared electrons are of course distinguished as before by enclosing the subgroups or grouplets of the same group (that is, with the same principal quantum number) in brackets : e. g. (2, 2, 4) for the complete second quantum group of $2\times2_{11}$, $2\times2_{21}$, and $4\times2_{22}$ electrons.

cal values of the effective atomic number, which tells us how many electrons the atom has in the compound, and how many of them are shared. If our general views of valency are correct, and if we have correctly interpreted the structure of the molecule, the calculation up to this point does not admit of any doubt.

The next question is what we can do to distribute these electrons into groups in accordance with the laws which Bohr has shown to determine the arrangements in isolated atoms. Here of course we are on more uncertain ground. The only sound principle is to adhere as closely as we can to the physical conclusions, and make no new hypotheses that we can avoid. The sharing of the valency electrons may be assumed to make no difference to the distribution of the unshared so far as the lowest quantum groups are concerned. These will be filled in the same way as in the isolated atom. For example, in $K_2[PtCl_6]$ the effective valency of the platinum is 8_6, and hence its E.A.N. is 86_6. Thus it has $86 - 2\times6 = 74$ unshared electrons. No one would dispute that 2 of these 74 are in the first quantum group, 8 in the second, and 18 in the third : this makes 28, and leaves 46 to be accounted for. Since the fourth quantum group of 32 is filled up in the uncombined atom at Lu 71, it is practically certain that by the time we reach Pt 78, with 7 more units of positive charge on the nucleus, it will be too firmly fixed for the number of its electrons to be modified by the presence of the shared electrons. We may therefore assign 32 more electrons to this fourth group, leaving 14, of whose positions we know nothing except that certainly some, and very likely all, occupy 5-quantum orbits. We can thus sum up our conclusions in the symbol

$$\text{Pt in } K_2[PtCl_6] = 86_6 = (2)\ (8)\ (18)\ (32)\ (14)\ \underline{6},\ \underline{6}.$$

Potassium platinichloride is a stable compound, and so this must be a stable arrangement of electrons ; it is not readily increased by reduction or diminished by oxidation ; but whether this stability of the 14 unshared electrons is due to their number alone (together with the nuclear charge), or depends on the presence of the 12 shared electrons [1]—in other words whether we

[1] The remarkable stability of a group of 12 shared electrons—of a covalency of 6—is already sufficiently obvious, and has been so ever since the early days of Werner's theory ; but we are more immediately concerned with the stability of the unshared group of 14 which is associated with it in compounds of this type.

should regard the (14) $\underline{6}$, $\underline{6}$ as analogous to a single Bohr group, or to two such groups—we do not yet know, although the examination of the chemical evidence and comparison with the E.A.N.'s of this and similar elements in other compounds may be expected to throw light on the point.

I have intentionally chosen a rather complicated example, and one in which the result has no obvious symmetry, in order to show that the method expresses the known facts with the minimum of assumptions. The only assumption made about the shared orbits is that they differ in some way from the unshared : their division into two equal quasi-subgroups is merely to indicate their invariable occurrence in pairs. If it is asked what advantage we gain by constructing these formulae the answer is that it is only in some such way as this that we can register the stable electronic constitutions of different atoms, and so discover how the stability is related to the structure. In the platinichlorides we find stable arrangement of 14 unshared electrons along with 12 shared. By comparison with similar formulae for the atoms in other compounds we may find how far this grouping is generally stable, and how far its occurrence in the platinichlorides is determined by one or other of the factors present in that particular type of molecule : the covalency, the nature of the attached groups, or the periodic group or horizontal period to which platinum belongs. We thus find, for example, that (with some doubtful exceptions) the 4-covalent platinum compounds such as $K_2[PtCl_4]$ (84_4 = (2) (8) (18) (32) (16) $\underline{4}$, $\underline{4}$) do not have 14 but 16 electrons in this group : that iridium forms a compound $K_3[IrCl_6]$ in which it has the same E.A.N. as platinum in the platinichlorides, but that osmium does not do so : that in the next triad likewise the two last elements, rhodium and palladium, form similar compounds $K_3[RhCl_6]$ and $K_2[PdCl_6]$, but not ruthenium : and that in the first triad it is the first two elements, iron and cobalt, which behave in this way (as in $K_4[Fe(CN)_6]$ and $K_3[CoCl_6]$), and not the third, while chromium is remarkable for giving a series of complex derivatives closely related (often even in colour) to these cobalt compounds, such as $K_3[CrCl_6]$, in all of which it has 11 electrons in the place of these 14. These examples are only mentioned to show that this method of formulation is of use in comparing in detail the properties of elements throughout the periodic table.

Many examples work out more symmetrically than these,

especially when we are not dealing with the transition elements (in the wider sense). The elements of the first four periodic groups, in their normal compounds with the group covalency, all give a number of unshared electrons either equal to that of an inert gas (typical elements and A subgroups) or 8 less (i. e. with the last electron group of the inert gas removed : B subgroups), and we are obviously justified in arranging these numbers as in the inert gases. For example :

Mg in $Mg\langle^{Et}_{I}$	$12+2$	$= 14_2$	=	(2) (8) $\underline{2}$, $\underline{2}$
B in BCl_3	$5+3$	$= 8_3$	=	(2) $\underline{3}$, $\underline{3}$
C in CH_4	$6+4$	$= 10_4$	=	(2) $\underline{4}$, $\underline{4}$
Si in $Si(CH_3)_4$	$14+4$	$= 18_4$	=	(2) (8) $\underline{4}$, $\underline{4}$
Ti in $TiCl_4$	$22+4$	$= 26_4$	=	(2) (8) (8) $\underline{4}$, $\underline{4}$
Zn in $Zn(C_2H_5)_2$	$30+2$	$= 32_2$	=	(2) (8) (18) $\underline{2}$, $\underline{2}$
In in $InCl_3$	$49+3$	$= 52_3$	=	(2) (8) (18) (18) $\underline{3}$, $\underline{3}$
Sn in $SnCl_4$	$50+4$	$= 54_4$	=	(2) (8) (18) (18) $\underline{4}$, $\underline{4}$
Pb in $Pb(C_6H_5)_4$	$82+4$	$= 86_4$	=	(60) (18) $\underline{4}$, $\underline{4}$

(It is obviously convenient in dealing with large numbers not to write out the earlier groups in full every time, and, as in the last example, we may use the symbols (10), (28), (60) for the completely filled groups of the first two, three, or four quantum numbers.)

At this point we may consider whether any relation can be found between the Bohr electronic structures and the covalency rule. On the Bohr system in its recently modified form, while the successive sizes of the groups (with the same first quantum number) are 2, 8, 18, 32 ($2n^2$, where n is the first quantum number), those of the subgroups (with the same first and second quantum numbers) are 2, 6, 10, and 14 (i. e. $4n-2$), and those of the grouplets (with all three quantum numbers the same) 2, 4, 6, 8 (i. e. $2n$). We might expect that the number of shared electrons, which is twice the covalency, would follow one or other of these divisions, in which case the successive covalency maxima would be, if they corresponded to the groups, 1, 4, 9, 16 : if to the subgroups, 1, 3, 5, 7 : and if to the grouplets, 1, 2, 3, 4. None of these relations holds : on the contrary we find that the values of the covalency maxima themselves correspond to the sizes of the grouplets (2, 4, 6, 8). (This rather surprising result, that the number of pairs of shared electrons is to be compared with the number of electrons in a grouplet, is some justification for

writing the former as we have done in the form of two equal grouplets ($\underline{n}$, $\underline{n}$).) In the isolated atom the grouplets of these sizes form the completion of the successive quantum groups, and if there is a real relation between the grouplets and the covalencies, this should show itself by the positions in the series of elements at which the two phenomena first appear. That there is such a relation is seen if we examine the effective atomic numbers of a series of atoms in compounds in which they exhibit a high covalency, and compare them with those given by imaginary compounds whose formation, otherwise possible, is forbidden by the covalency rule. These are shown in the following table (A = the radical of acetylacetone, $C_5H_7O_2$).

I. Actual.

H in [F–H←F]	4_2	= $\underline{2}$, $\underline{2}$
Be in BeA_2	10_4	= (2) $\underline{4}$, $\underline{4}$
C in CCl_4	10_4	= (2) $\underline{4}$, $\underline{4}$
Al in AlA_3	22_6	= (2) (2, 2, 4) $\underline{6}$, $\underline{6}$
Si in $[SiA_3]X$	22_6	= (2) (2, 2, 4) $\underline{6}$, $\underline{6}$
S in SF_6	22_6	= (2) (2, 2, 4) $\underline{6}$, $\underline{6}$
Ti in $[TiA_3]X$	30_6	= (2) (2, 2, 4) (2, 2, 4) $\underline{6}$, $\underline{6}$
Zr in ZrA_4	52_8	= (2) (2, 2, 4) (2, 2, 4, 4, 6) (2, 2, 4) $\underline{8}$, $\underline{8}$

II. Non-existent : forbidden by covalency rule.

B in BA_3	14_6	= (2) $\underline{6}$, $\underline{6}$
Si in SiA_4	26_8	= (2) (2, 2, 4) $\underline{8}$, $\underline{8}$
Ti in TiA_4	34_8	= (2) (2, 2, 4) (2, 2, 4) $\underline{8}$, $\underline{8}$

It is obvious that the distinction between the structures of the possible and those of the impossible compounds is this. The covalency cannot exceed by more than two the number of the largest (unshared) grouplet in the atom : the series of even numbers which is formed by the concluding grouplets of the successive quantum groups is continued by the maximum covalency number. Thus in compounds of hydrogen, where there are no unshared electrons, the maximum covalency is 2 : in the first short period the only complete unshared group is that of 2, and the maximum covalency is 4 : after neon (2) (2, 2, 4) the 4-grouplet of the second quantum group is established, and a covalency of 6 becomes possible. So far the new covalency limit always appears as soon as we should expect it, but the beginning of the covalency of 8, if we have placed it correctly, is rather

later than we should have anticipated. The 18 group, with its grouplet of 6, is firmly established by the time we reach zinc (30), and germanium (32) might form a tetra-acetylacetonate GeA_4, in which it would have the structure $32 + 12 = 44_8 = (2)$ (2, 2, 4) (2, 2, 4, 4, 6) **8**, **8**, which seems permissible. So too selenium in its hexafluoride SeF_6 ($34 + 6 = 40_6 = (2)$ (2, 2, 4) (2, 2, 4, 4, 6) **6**, **6**) should be capable of rising to a covalency of 8, and hence of accepting two more pairs of shared electrons, in which case it would be hydrolyzed by water. The evidence, as we have seen, is that this germanium compound cannot be formed, and that selenium hexafluoride is unaffected by water, and so must contain selenium in its highest state of covalency. It follows that a covalency of 8 is not possible in the second half of the first long period (Cu 29 to Br 35), but only when we reach the second long period (after Kr 36), when we find for example ZrA_4, whose E.A.N. is given in the table above. It would therefore seem that while covalencies of 4 and 6 become possible as soon as the 1- and 2-quantum groups respectively are filled with unshared electrons, that of 8 cannot begin as soon as the 3-quantum group of 18 is full, but only when the atom has an unshared group of 8 in addition, or, as we probably should put it, when the nuclear charge is at least 8 units larger than corresponds to the completion of the third quantum group. As we shall see shortly, this is in accordance with the principles of the Bohr structures.

We can therefore express the covalency rule in terms of the structure by saying that a covalency of $2n + 2$ does not become possible until there are enough unshared electrons in the atom to fill completely the first n quantum groups : with this further qualification, that covalencies of 2, 4, and 6 begin as soon as this condition is fulfilled, but that of 8 only some 8 places later.[1]

[1] The strict application of this rule would indicate that when the fourth-quantum group of 32, with its grouplet of 8, was completed (after lutecium 71, at the end of the rare earth metals), a covalency of 10 would be possible, although to judge from the behaviour of the 8-covalent compounds we should expect its occurrence to be rare, and its beginning to be considerably delayed. The only definite argument in favour of its existence is the fact already mentioned, that osmium octofluoride is hydrolyzed by water, which suggests that the covalency of osmium is not limited to 8. In this connexion the hydrates of the acetylacetonates of zirconium, cerium, and hafnium, ZrA_4, CeA_4, and HfA_4 should be noticed. (Zr : Biltz and Clinch, *Z. anorg. Chem.* 1904, **40**, 218. Ce : Job and Goissedet, *C. R.* 1913, **157**, 50. Hf : v. Hevesy and Lögstrup, *Ber.* 1926, **59**, 1890.) The zirconium and hafnium compounds contain 10 molecules of water, the cerium compound

It is to be observed that there is a marked difference between the grouping of shared and unshared electrons, in that the former are able to form large groups with a smaller nuclear charge than would be required by the latter. In the Bohr structures grouplets of 6 do not begin until we reach copper (29), with a nuclear charge one unit greater than corresponds to the completion of the third quantum group of 18. But a covalency of 6 (which presumably involves something like a grouplet of 6 shared electrons) is found as early as aluminium (13) and even sodium (11), where the total number of electrons in the combined atom (E.A.N. 22_6) greatly exceeds the nuclear charge. If we suppose every shared electron to count as a half, the atom in both cases has the equivalent of 16 electrons—3 and 5 more than corresponds to its atomic number : and yet the grouping is stable, while a simple anion such as $[Co]^-$ (E.A.N. 28_0 = (2) (8) (18)), in which the grouplet of 6 would be completed, cannot exist owing to the instability of the (unshared) 18 group in so weak a positive field.

As the covalency increases, the need of a greater charge on the nucleus seems to make itself felt : and this no doubt is the reason why the appearance of the covalency of 8 is delayed.

Pure and Mixed Valency Groups

Among the electrons of the combined atom it is convenient to distinguish those of the core from those of the valency group. The core is composed of the inner groups of unshared electrons which take no direct part in the chemical combination : the

is stated to contain 11, which is within possible experimental error of 10. There is no question of the hydration of metallic ions, since the compounds are not ionized, and no other diketone derivatives containing anything like this amount of water are known. These hydrates are obviously of an unusual type : they are formed by preparing the acetonylacetonate in aqueous solution, but when once the water has been removed (as by recrystallization from absolute alcohol) it cannot be replaced. It is conceivable that the atoms of these metals, having completed their valency groups of 16 shared electrons by combination with the diketone radicals in the usual way, then form a further group of 20 by co-ordination with 10 molecules of water :

ZrA_4, $10H_2O$: 72_{8+10} = (2) (2, 2, 4) (2, 2, 4, 4, 6) (2, 2, 4) (8, 8) (10, 10)

CeA_4, $10H_2O$: 90_{8+10} = (28) (2, 2, 4, 4, 6) (2, 2, 4) (8, 8) (10, 10)

This suggestion, in the present state of our knowledge, does not seem very probable, and no parallel instances have yet been found ; but the facts are worth noting.

valency group consists of all the shared electrons, and any unshared which are not accommodated in the inner groups. If the valency group contains both kinds, shared and unshared, it is called mixed, if one kind only, pure. Completely unshared valency groups occur only in isolated atoms or monatomic ions, and do not concern us here, so that by pure groups we mean those in which all the electrons are shared.

The methods by which we can form an idea whether all the unshared electrons are included in the core, or whether some of them form part of the valency group, are best illustrated by a series of examples. On the Bohr theory, as we have seen, the valent [1] elements fall into two classes. In the **first** of these all the quantum groups are complete [2] except the highest. This last is then the valency group of the isolated atom, and we may assume that in the formation of compounds the lower groups are unaffected (as regards their size) and remain filled with unshared electrons. They constitute an unalterable core, and the valency (apart from certain limited exceptions to be considered later) either is constant, or changes by two units at a time owing to rearrangements of the valency electrons, as in the change from trivalent to pentavalent nitrogen. The **second** class of elements consists of those (enclosed in frames in the table, p. 39) in whose atoms not only the highest quantum group but also the next (in the rare earth metals the next two) is imperfectly filled, containing some number intermediate between two stable values (8 and 18, or 18 and 32). In such atoms the valency group is not fixed, as one or more electrons from the next incomplete group may be utilized for chemical combination. This leads to valencies varying by single units, to the formation of coloured and paramagnetic ions, &c. These are the transition elements in the wider sense.

In atoms of this last class it is difficult to tell with any certainty what is the size of the valency group, as we do not know how many electrons from the next group may be drawn into it ;

[1] This convenient term may be used for those elements which exhibit valency, i. e. all but the inert gases.

[2] By ' complete ' is meant that they have attained a size which gives them great stability, not necessarily that they have reached their maximum size of $2n^2$ (where n is the principal quantum number). As we have seen, a group of 8 or 18 electrons has this stability, even when it can ultimately expand to 18 or 32 : for example, the fourth quantum group contains 8 electrons in krypton, 18 in xenon, and 32 in emanation. Any group of 8, 18, or 32 electrons may thus be called complete.

but in those of the first class, with completed quantum groups, the electrons required to fill these inner groups cannot be called upon to act as valency electrons, and so the size of the core is fixed and known. Hence in the compounds of the first class of elements we can reach a definite conclusion as to whether there are any unshared electrons outside these inner groups, and if so, how they are related to the number of shared electrons.

This may be illustrated from the elements of the second short period, which ranges from neon (2) (8) to argon (2) (8) (8), the intermediate elements having from 1 to 7 electrons in the third quantum group. The core of 10 electrons = (2) (8) is very stable, and can scarcely be broken into by any means, certainly not by chemical combination. So in the compounds of these elements we know that we have to assign 10 unshared electrons to the first two quantum groups, which are then full and cannot hold any more. Any additional unshared electrons must lie outside these two groups, and may be supposed to form along with the shared electrons a separate organization having its own rules of stability, the valency group.

Of the earlier members of this period, which are metals, we may consider magnesium 12 = (2) (8) (2). This forms the non-covalent ion $[Mg]^{++}$ (if we assume it unhydrated), in which the two valency electrons are gone, and the core alone remains. It also forms di-covalent compounds such as $MgEt_2$ and MgEtI, and by co-ordination it can assume covalencies of 3, 4, and 6 :

$[Mg]^{++}$	$12-2$	$= 10_0$	$= (2)\ (8)$
$CH_3–Mg–I$	$12+2$	$= 14_2$	$= (2)\ (8)\ \underline{2},\ \underline{2}$
$(C_2H_5)_2O\rightarrow Mg\langle^{CH_3}_{I}$	$12+4$	$= 16_3$	$= (2)\ (8)\ \underline{3},\ \underline{3}$
$(C_2H_5)_2O\searrow$ / $(C_2H_5)_2O\nearrow Mg\langle^{CH_3}_{I}$	$12+6$	$= 18_4$	$= (2)\ (8)\ \underline{4},\ \underline{4}$
$[Mg(OH_2)_6]Cl_2$	$12+2\times6-2$	$= 22_6$	$= (2)\ (8)\ \underline{6},\ \underline{6}$

So with aluminium we get, amongst others, forms like these :

$[Al]^{+++}$	$13-3$	$= 10_0$	$= (2)\ (8)$
$Al(CH_3)_3$	$13+3$	$= 16_3$	$= (2)\ (8)\ \underline{3},\ \underline{3}$
$Na_3[AlF_6]$	$13+6+3$	$= 22_6$	$= (2)\ (8)\ \underline{6},\ \underline{6}$

and with silicon :

SiH_4	$14+4$	$= 18_4$	$= (2)\ (8)\ \underline{4},\ \underline{4}$
$K_2[SiF_6]$	$14+6+2$	$= 22_6$	$= (2)\ (8)\ \underline{6},\ \underline{6}$

In all these examples we have found, besides the core of 10, nothing but shared electrons—4, 6, 8, and 12 according to the covalency. This is what is meant by a pure valency group. It is evident that with a stable core such a group is reasonably stable whatever its size (provided that it is even, and does not exceed the covalency limit for the atom), though the chemical behaviour shows that particular sizes such as 8 and 12 are more stable than 2, 4, or 6 : that is, that covalencies of 4 or 6 are more stable than those of 1, 2, or 3.

The next element is phosphorus. This gives three types of compounds, with covalencies of 3, 4, and 5 (6 does not seem to have been observed), as in PH_3, $[PH_4]I$, and PF_5.

PH_3	$15+3$	$= 18_3$	$= (2)\ (8)\ 2, \underline{3}, \underline{3}$
$[PH_4]I$	$15+4-1$	$= 18_4$	$= (2)\ (8)\ \underline{4}, \underline{4}$
PF_5	$15+5$	$= 20_5$	$= (2)\ (8)\ \underline{5}, \underline{5}$

With sulphur we find (in addition to certain anomalous compounds) covalencies of 0, 1, 2, 3, 4, and 6 :

$[S]^{--}$	$16+2$	$= 18_0$	$= (2)\ (8)\ (8)$
$[C_2H_5\text{–}S]K$	$16+1+1$	$= 18_1$	$= (2)\ (8)\ 6, \underline{1}, \underline{1}$
$(C_2H_5)_2S$	$16+2$	$= 18_2$	$= (2)\ (8)\ 4, \underline{2}, \underline{2}$
$[(C_2H_5)_3S]I$	$16+3-1$	$= 18_3$	$= (2)\ (8)\ 2, \underline{3}, \underline{3}$
$H_2\left[\begin{matrix}O\\O\end{matrix}\!\!\searrow\!\!\swarrow\!\!\begin{matrix}S\\\end{matrix}\!\!\begin{matrix}\swarrow O\\\searrow O\end{matrix}\right]$	$16+2$	$= 18_4$	$= (2)\ (8)\ \underline{4}, \underline{4}$
SF_6	$16+6$	$= 22_6$	$= (2)\ (8)\ \underline{6}, \underline{6}$

It will be seen that with covalencies of 4 and 5 in phosphorus, and of 4 and 6 in sulphur, we again get pure (wholly shared) valency groups ; but with those of 1, 2, and 3 we have quite a different arrangement, the total number of electrons outside the core being always 8, of which 2, 4, or 6 may be shared, the rest being unshared : the stability of the group seems to depend only on its total number. This is an example of mixed valency groups, and constitutes the famous octet.[1]

The octet has been so much discussed, and is found in so many familiar compounds, that we are inclined to regard it as the typical valency group, and to imagine that a group of valency electrons, whose stability is determined by its total

[1] In writing the E.A.N. it is convenient to include all the electrons of the octet in one bracket, as in (6, 1, 1), (4, 2, 2), &c. This is merely to simplify the counting, and does not imply the assumption of any quantum relation between the shared and the unshared electrons of the octet.

number, with little reference to whether the individual electrons are shared or not, is the normal state of things. The facts however are quite otherwise: the mixed group is rather the exception than the rule, even among atoms with a covalency less than 4. It is obvious that a mixed octet cannot occur in the elements of the first three periodic groups. These elements are limited in their valency by the number of electrons which they have to offer, and even by sharing all of them normally, and so doubling their number, they cannot form a complete octet, much less one in which there are unshared electrons: their incomplete octets are indeed unsaturated, and tend to complete themselves, as we have seen, by co-ordination, but in so doing they form not a mixed but a wholly shared group. The atoms might no doubt complete their octets by taking up unshared electrons and so becoming anions, as in the imaginary compound $K_2[BCl_3]$, in which the sextet of the tri-covalent boron would be increased to 8 (2, $\underline{3}$, $\underline{3}$) by two electrons taken from the potassium, but such compounds are never formed. The elements of the fourth periodic group, having 4 valency electrons, form an octet directly, but this of course is wholly shared.

The mixed octet is therefore confined to the elements of groups V, VI, VII, and possibly VIII, and even here is not found, so far as can be ascertained, in the A subgroups (V, Nb, Ta: Cr, Mo, W, U: Mn: and the transitional triads forming group VIII). The size of the core in these A elements is of course variable, but the stable sizes for each element can be discovered by examining its compounds, and if the mixed octet occurred we ought to find that there was a tendency for the atoms, when their covalency was less than 4, to have a total E.A.N., irrespective of the covalency, 8 units greater than a stable form of core. No such tendency is however observed, although a pure octet, that is, a covalency of 4, is common enough.

When we come to covalencies of more than 4, we find few signs of any tendency for unshared electrons to form part of the group. Not only are the stable groups of 12 or 16 electrons wholly shared, but, which is very surprising, there seems to be no tendency [1] for the odd covalencies of 5 and 7, that is, groups of 10 and 14 shared electrons, to make themselves up to the

[1] Certain exceptions are found in which an apparently inert pair of valency electrons occurs; but these, which will be discussed later, are not more frequent with odd than with even covalencies.

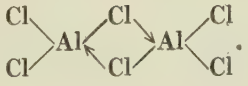
apparently more stable numbers of 12 or 16 by the addition of a pair of unshared electrons. On the contrary the exceptional prevalence of a covalency of 5 in the fifth group, as in PF_5, indicates that the stability of 10 shared electrons is greater when there are no unshared electrons present in the group with it.

The conclusion therefore is that while purely shared groups of any even number from 2 to 16 are possible, a mixed group can only (or almost only) occur when its total number is 8, and even then only when it makes up the E.A.N. of the atom to that of an inert gas, with the result that it is confined to elements a few places before such a gas. The great stability of the inert gas structures seems to make possible a co-operation of the shared with the unshared electrons, so that when an atom reaches this number it acquires a stability to some extent independent of how many of the electrons are shared.

The exceptional character of a group of 8 electrons is indicated by the remarkable stability of the wholly shared octet. Examples of this have already been given in the behaviour of the ammonium as compared with the oxonium compounds, in the stability of the ions XO_4 of the phosphates, sulphates, perchlorates, chromates, &c., and in the 4-covalent chelate compounds of sodium and thallium (p. 146). A further proof is afforded by the comparison of the covalent halides of the third periodic group with those of the typical and B elements of the fourth. The trihalides (with the exception of those of boron) are always less volatile than the heavier tetrahalides, as the following list of boiling-points shows :

BCl_3	$AlCl_3$	$FeCl_3$	$GaCl_3$		
18°	183°	280°	220°		
CCl_4	$SiCl_4$	$TiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
78°	58°	136°	86·5°	114°	(M. Pt. −15°)

The difference is due to association of the trichlorides (those of aluminium, iron, and gallium have been shown to give double molecules in the vapour), while the tetrahalides show no sign of association. It is evident that the trivalent elements, having incomplete octets, strive to complete them by co-ordination, the metal acting as acceptor and the halogen as donor : thus Al_2Cl_6 is presumably



The tetrahalides might behave in the same way, since (with the exception of carbon) the elements can assume a covalency higher than 4: but the covalency of 4 is so stable that this does not happen.[1]

The presence of this group (4, 4) is no doubt an important factor in the stability of the carbon compounds, and explains why carbon can scarcely be induced to form an anion $[CR_3]^-$, in which the octet, though it would still be complete, would not be fully shared.

The Atomic Core

Having seen what are the stable forms of the valency group we have next to consider the core; for it is these two factors which between them determine the stability of the combined atom, and so that of the whole molecule. Among the transition elements in the wider sense, where several different cores are possible for the same element, this is a very complicated question, and is better discussed in connexion with the individual elements. But even here we can see the importance of the core in determining the state of the atom. With iron, for example, we find two states of the core running through the whole of the compounds, from the simple ions to the most highly covalent derivatives: in one of these the core is composed of 24 and in the other of 23 electrons:

Fe: 26 = (2) (8) (14) (2)

Ferrous: Fe^{++}: 24_0 = (2) (8) (14)

$K_4[Fe(CN)_6]$: $26+6+4 = 36_6$ = (2) (8) (14) 6, 6

Ferric: Fe^{+++}: 23_0 = (2) (8) (13)

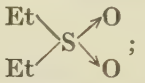
$K_3[Fe(CN)_6]$: $26+6+3 = 35_6$ = (2) (8) (13) 6, 6

In the same way we find among the compounds of copper the cuprous core of 28 = (2) (8) (18) and the cupric of 27 = (2) (8) (17). The current terminology of these complex compounds, in which this difference of core is recognized (under the name of a difference of valency) as the basis of the classification of the compounds of a given element, shows how useful the distinction is. The numerical value of the valency is on this system the difference between the number of electrons in the core and the number in the isolated atom.[2]

[1] The remarkably low volatility of zirconium tetrachloride, which boils at a red heat, may possibly be due to a polymerization of this kind.

[2] It should be noticed that certain modifications of structure which are often difficult to determine in practice leave the core unaffected. A co-

Among the elements less far removed from (usually not more than 6 places before or 3 after) the inert gases, more definite conclusions can be reached. The core is normally composed of complete groups, and its number is that of an inert gas or 8 less (0, 2, 10, 18, 28, 36, 46, 78, 86). The maintenance of a fixed core is however compatible with certain changes of valency in the ordinary sense of that term, many of which have already been pointed out. The core of the nitrogen atom is 2 in ammonia and in the ammonium ion: that of silicon is 10 in the tetrahalides and in the fluosilicates: that of sulphur is 10 in diethyl sulphide $\begin{matrix}\mathrm{Et}\\\mathrm{Et}\end{matrix}\!\!>\!\mathrm{S}$, in diethyl sulphoxide $\begin{matrix}\mathrm{Et}\\\mathrm{Et}\end{matrix}\!\!>\!\mathrm{S}\rightarrow\mathrm{O}$, and in diethyl sulphone



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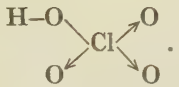
and that of chlorine 10 in ethyl chloride Et–Cl, in chlorous acid H–O–Cl→O, in chloric acid H–O–Cl$\begin{matrix}\nearrow\mathrm{O}\\\searrow\mathrm{O}\end{matrix}$, and in perchloric acid



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It will be noticed that on the old conception of valency, in which no distinction was made between covalency and electrovalency, and the co-ordinate link to oxygen was written as a double bond, all these changes require an alteration of the valency by an even number: thus in the above examples the valency of nitrogen changes from 3 to 5, that of silicon from 4 to 8 (if the fluosilicate is regarded as a true complex salt), that of sulphur from 2 to 4 and 6, and that of chlorine from 1 to 3, 5, and 7. All these changes involve the formation of co-ordinate links; but there is another series (also without alteration of core) arising through the possibility of the mixed octet.

ordinate link in which the atom acts as acceptor has no effect: the core is the same in the simple and in the dimeric form of aluminium chloride, and indeed the same also in the aluminium ion, whether it is hydrated or not. Again in double salts it is often impossible to be certain whether the components really form a complex molecule, or only a crystalline aggregate; but this does not affect the size of the core, which is the same, for example, in $PbCl_4$, as it is in $K_2[PbCl_6]$. Also the doubt whether, say, an oxygen atom is united by a double link or a co-ordinate link (for example, in trimethylamine oxide) is unimportant from this point of view: the core is 2 both in $R_3N{=}O$ and in $R_3N{\rightarrow}O$. These differences all affect the covalency, but not the core.

The elements of the later groups may, if the covalency rule permits, use all their valency electrons for the formation of a number of normal covalencies equal to the group-number, as in PF_5 and SF_6. But if they form mixed octets, their valencies instead of being n (group-number) are $8-n$ (in groups V, VI, and VII 3, 2, and 1): here again the difference $(n-(8-n) = 2n-8)$ is necessarily an even number.

But of the observed changes of valency in these elements a considerable number involve a real alteration of the core, nearly always (apart from copper and gold, where the instability of the core has already been explained) in the direction of an increase, there being more unshared electrons in the atom than we should expect. Some of these are isolated instances, which are better discussed under the elements in question, as in the 'odd molecules' NO, ClO_2, and $InCl_2$. Others again throw little light on the stability of atomic structures, because the properties of the molecules in which they occur show that these structures are in fact highly unstable: as in the compounds of trivalent carbon, to which those of divalent nitrogen and univalent oxygen may now be added.[1] These may be called 'forced' valencies: they indicate an unstable electronic grouping which rearranges itself as soon as it has an opportunity of doing so. There is however one considerable class of abnormal valencies which can be recognized as being due to some common cause, that, namely, in which two of the valency electrons appear to have become inert, as though they had been absorbed into the core. This phenomenon is first to be noticed in group III B in InCl, and more markedly in the thallous compounds: in the typical and B elements of group IV it is especially prominent, from the divalent compounds of carbon to those of germanium, tin, and lead. In group V B we find it in antimony and still more in bismuth, in VI B in sulphur, selenium, and tellurium, and in VII B in iodine and bromine and possibly in chlorine. Thus it is most marked in the fourth group, and is generally prevalent among the heavier B elements. It is especially evident in the series of elements following gold: mercury, thallium, lead, and bismuth. The new development of the Bohr theory due to Stoner and Main Smith indicates a possible reason for this peculiarity. We now realize that the first two electrons in any group, forming the grouplet N_{11}, correspond to the pair of 1_{11} electrons in helium, and can have a certain completeness of

[1] Perhaps chlorine dioxide should be included under this head.

their own, approaching that which they have in helium, where they form a complete group. We might thus anticipate that under some conditions the first two valency electrons of an element could become more like core-electrons, and refuse either to ionize, or to form covalencies, or both.[1] How their presence in this state would react on the rest of the valency group—whether they would have to be counted as part of it, or would change the conditions of its stability, or finally should be regarded as having no connexion with it and genuinely forming a separate group of the core—cannot at present be predicted; but something may be learnt by examining the chemical facts. Why this inertness of the N_{11} pair should appear precisely where it does in the periodic table, we cannot say: the spectral evidence supports the chemical, but no reason has been assigned for either. The property shows a singular development in the successive elements mercury, thallium, lead, and bismuth, with the structures:

Orbits	.	5	6_{11}	6_2
Hg 80	= (60) (18)	2		
Tl 81	= (60) (18)	2	1	
Pb 82	= (60) (18)	2	2	
Bi 83	= (60) (18)	2	3	

The normal valencies should of course be mercury 2: thallium 3: lead 4: bismuth 5, or in octet formation 3. The actual valencies in the salts appear to be mercury 1 and 2, thallium 1 and 3, lead 2, and bismuth 3—in each case less, and in all but that of mercury 2 less, than we should expect: two of the valency electrons seem to be under some conditions capable of remaining unshared and unionized. But a closer inspection shows that there is a remarkable change in the character of the inertness. In the earlier members of the series the 6_{11} pair can be shared although they cannot, or can only with difficulty, be ionized. Mercurous mercury is not really univalent. The ion, as has been abundantly proved, is not $[Hg]^+$ but $[Hg_2]^{++}$: each atom is using both of its valency electrons, but one is shared with the other atom giving $[Hg-Hg]^{++}$, the E.A.N. of the atom thus being

$$80 + 1 - 1 = 80_1 = (60)\ (18)\ \underline{1},\ \underline{1}.$$

The strong tendency for these electrons to serve rather for

[1] See Grimm and Sommerfeld, *Z. f. Phys.* 1926, **36**, 36: but many of their examples of change of valency are of the kind which have been explained above without assuming a change of core.

covalencies than for electrovalencies is shown by their being able to link the two metallic atoms together, a structure which is almost unique. That this tendency extends to both the valency electrons of the mercury is proved by the very small ionization of mercuric salts,[1] which, on the principles we have already accepted, indicates that the equilibrium in the reaction $HgX_2 \rightleftharpoons [Hg]X_2$ is very far on the left-hand side. The small ionization of the mercuric salts, together with their slight tendency to complex formation, points to a further peculiarity presumably due to the same cause as the inertness of the N_{11} pair. The mercury in the covalent compound X—Hg—X (as in the chloride or cyanide) has only a quartet of shared electrons, which in this element seems to be quite stable, although it would normally be highly unsaturated: compare for example the very unstable $ZnEt_2$ with the stable $HgEt_2$. A somewhat similar peculiarity occurs in the compounds of divalent carbon, in which the E.A.N. is (2) (2, $\underline{2}$, $\underline{2}$): these are far less unsaturated than we should expect from the extraordinarily strong tendency of the carbon to maintain its octet: the recently discovered methylene diacetal[2] Et–O–C–O–Et (B. Pt. 77°: vapour density normal) is not attacked by bromine, and only slowly by alkaline permanganate. It is to be noticed that by the time we reach lead, the stability of this (2, $\underline{2}$, $\underline{2}$) group has disappeared: the simple covalent compounds always have a complete shared octet.

The same inertness is shown even more strongly by thallium, where we have the thallous ion $Tl^+ = 80_0$ = (60) (18) 2: this has been shown to be partly polymerized like the mercurous ion to $[Tl_2]^{++}$, presumably $[Tl{=}Tl]^{++}$, in which one of the three electrons of each atom is ionized, and the other two are shared. The univalency is almost limited to the ion and the liquid alkylates such as Tl—O–Et, where we have the E.A.N. 82_1 = (60) (18) (2) $\underline{1}$, $\underline{1}$: the compounds of higher covalency (2, 3, 4, and 6) nearly always involve the use of all three electrons, having E.A.N.'s of the form (60) (18) $\underline{n}$, $\underline{n}$. It is remarkable that although thallium readily forms alkyl derivatives of great stability, none are known of the types TlAlk or $Tl(Alk)_3$: they are all salts of the type $[Tl(Alk)_2]X$, with a quartet of shared electrons as in the mercury alkyls.

[1] The mercuric salts of organic acids are as a rule ionized in water to about the same extent as the acids from which they are derived: the halides of course much less.

[2] Scheibler, *Ber.* 1926. 59, 1022.

Lead shows this peculiarity in its most marked form: it is divalent in all its simple salts, and quadrivalent in all its stable alkyl and aryl compounds:

$[Pb]Cl_2$ $82-2 = 80_0 = (60)\,(18)\,2$
$Pb(CH_3)_4$ $82+4 = 86_4 = (60)\,(18)\,\underline{4},\,\underline{4}$

So it appears that of the 4 electrons outside the stable core of 78 two alone can be removed by ionization, while all 4 are available for conversion into covalencies.

In bismuth two of the 5 electrons outside the core seem to have become inert for nearly all purposes. Except in a few organic derivatives bismuth never attains a valency of more than 3. Since the majority of the familiar bismuth compounds are tri-covalent, it might be argued that this is merely an example of the formation of a mixed octet (2, $\underline{3}$, $\underline{3}$), and this may perhaps be true of the tri-covalent compounds themselves: but no similar explanation can be given of the appearance of this pair of unshared electrons in derivatives in which the bismuth has covalencies of 4, 5, and 6, as may be seen by comparing the following effective atomic numbers:

$[PH_4]I$ $15+4-1 = 18_4 = (2)\,(8)\,\underline{4},\,\underline{4}$
$K[Bi(SO_4)_2]$ $83+4+1 = 88_4 = (60)\,(18)\,2,\,\underline{4},\,\underline{4}$
$SbCl_5$ $51+5 = 56_5 = (28)\,(18)\,\underline{5},\,\underline{5}$
$K_2[BiCl_5]$ $83+5+2 = 90_5 = (60)\,(18)\,2,\,\underline{5},\,\underline{5}$

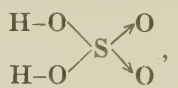
Even among the tri-covalent compounds such as the trihalides there is a marked difference in behaviour between those of bismuth and those of the lighter elements of the subgroup such as phosphorus and arsenic. The former have much more the character of salts of a $[Bi]^{+++}$ ion $80_0 = (60)\,(18)\,2$. They form a series of double salts with the halides of the more electropositive metals (such as that given above), and bismuth can replace the metals of group III A (lanthanum and the rare earth metals) in the peculiar double nitrates $M''_3[M'''(NO_3)_6], 24H_2O$. Both these properties are characteristic of elements with only three valency electrons.

Thus it appears that in the series of elements from mercury (80) to bismuth (83) the N_{11} electrons of the valency group first become reluctant to ionize, and finally will scarcely function as valency electrons at all. The further discussion of the peculiarities of this grouplet must be left until we come to deal with individual elements.

Definition of Absolute Valency

We have so far been engaged in disentangling the different forms of valency, in discovering their electronic mechanism, and in discussing the conditions of their formation. We can now describe the state of a combined atom in terms of its electrovalency, its normal covalency, and its co-ordination. It is worth considering what remains of valency in the older sense, as representing a state of the atom giving it a definite power of chemical combination. Can we speak absolutely of the valency of an atom in a compound, and if so, how can we define it in terms of the electronic structure ? No completely satisfactory answer can be given to this question. The modern distinction of different types of valency shows that the combining power of an atom may be due to more than one cause and may arise in more than one way, and it is not possible to express all the variations of this power as numerical values of a single constant. This is largely due to the complications introduced by the existence of mixed valency groups. On the whole the best definition of absolute valency seems to be that adopted by Grimm and Sommerfeld,[1] that it is numerically equal to the number of electrons of the atom ' engaged ' (beansprucht) in attaching the other atoms. It is thus equal to the difference between the atomic number and the number of unshared electrons in the combined atom.

In atoms with pure valency groups, the unshared electrons constitute the core ; the valency is then the difference between the atomic number and the size of the core (with iron (26), for example, it is two for compounds with a ferrous core of 24, and three for those with a ferric core of 23) ; we thus retain the familiar terminology, and at the same time relate it to the electronic structure. In the simple anions the difference between the number of electrons before and after combination is negative : a fluorine atom with 9 unshared electrons becomes an ion $[F]^-$ with 10, and has a valency of 1. The definition will thus cover these atoms also. With octet formation it can still be applied ; it gives the same values of the valency as the older formulae, and like them it fails to distinguish the co-ordinate link from the true double link : thus in



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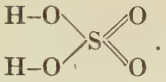
[1] *Loc. cit.*, p. 44

since 6 electrons of the sulphur are engaged[1] (one to each hydroxyl and two for each co-ordinate link), the valency is 6, as it was in the older symbol[2]



This method of designating the valency in octet compounds (2 for sulphur in H_2S, 6 in H_2SO_4), though familiar, involves abandoning for them the idea of the importance of the core, which only contains those electrons not counted towards the octet, and is the same (10), for example, in sulphur whether four (H_2S) or 8 (H_2SO_4) of the octet electrons are shared.

This definition gives a definitely wrong result when applied to such a molecule as the hydroxyl ion, in which an atom forms a covalency, and also receives an electron as an anion. Here the oxygen gains one of the two electrons it needs for the octet directly, and the other by sharing the electron of the hydrogen, to which it lends one of its own. Thus the number of its unshared electrons is the same as in the isolated atom, and so on the definition we have adopted its valency should be zero.

In general then it may be said that if a definition of absolute valency is needed, the best that can be given is that it is equal to the change in the number of unshared electrons caused by the combination. This leads in the majority of compounds to the numerical values to which we are accustomed, but in a few it breaks down entirely, while in most of those containing a mixed octet it fails to indicate the more important differences which the electronic theory detects. Where however the atom has a pure valency group, this definition expresses the changes in the core, which are the really fundamental characteristics of the atomic structure.

In order to show the results to which this definition leads, a series of values of the valency deduced from it may be given :

Hydrogen 1 in $H{-}CH_3$ and $[F{-}H{\leftarrow}F]^-$: boron 3 in BF_3 and $K[BF_4]$: aluminium 3 in $[Al]^{+++}$, $[Al,\ 6H_2O]^{+++}$, $Al(CH_3)_3$,

[1] The same is of course true of the ion $\left[\begin{matrix}O\leftarrow S\rightarrow O\\ O\end{matrix}\right]^{--}$: here the sulphur also has 8 shared electrons, but has received two of these as its anionic charge, so that it is using 6 of those which it had originally.

[2] The difference between the links $S\rightarrow O$ and $S{=}O$ is that while in both two electrons from the sulphur are shared by the oxygen, in the latter two additional electrons from the oxygen are also shared by the sulphur.

and Al_2Cl_6: silicon 4 in $SiCl_4$ and $K_2[SiF_6]$: lead 2 in $[Pb]Cl_2$, 4 in $Pb(CH_3)_4$ and $K_2[PbCl_6]$: nitrogen 3 in NH_3, 5 in $[NH_4]I$ and $CH_3\text{–}N\begin{matrix}O\\O\end{matrix}$: oxygen zero in $[H\text{–}O]^-$ and $[CH_3\text{–}O]^-$, 2 in $[O]^{--}$ and Et_2O, 4 in $[Et_2OH]Cl$: sulphur 2 in $[S]^{--}$ and Et_2S, 4 in $Et_2S\rightarrow O$, 6 in H_2SO_4 and SF_6: iodine 1 in $[I]^-$ and $I\text{–}CH_3$, 3 in $C_6H_5\text{–}I\begin{matrix}Cl\\Cl\end{matrix}$ and $[(C_6H_5)_2I]NO_3$, 5 in IF_5, and 7 in $(HO)_5I\rightarrow O$.

XI

SOLVATION

AN important group of co-ordination compounds consists of those which are formed by solutes with solvents. So far as the solutes are purely covalent, their solvation products do not call for special discussion ; but the combination of ionized molecules with solvents, and especially with water, is so frequent as to need further consideration : hydrated salts are the most familiar instances of co-ordination compounds in the whole of chemistry. Other hydroxylic solvents behave in the same way as water, and so also do ammonia and its substitution products, as was pointed out by Werner.[1] We have an immense amount of data as to the composition of the solids which are obtained from such solutions, and their study should be of great value in extending our knowledge of the factors which determine co-ordination. There are, however, as we shall see, considerable difficulties in interpreting these data, which in the present state of our knowledge can be only partially overcome. The most serious of these is the doubt whether all the solvent molecules which appear in the formula really form part of the molecular complex.[2]

If our theories of valency are true, they ought to be applicable to every kind of molecule. We have abandoned the idea of molecular compounds, and concluded that the forces which hold the constituent atoms of a molecule together must either be electrovalencies or covalencies ; and we have found these sufficient to account for all those molecules whose size can be definitely determined, either in the gaseous state or in solution. Now among the large number of recorded compounds of which the molecular weight cannot be determined, a considerable proportion are only known to exist from the facts that a solid phase can be produced which contains the elements in a proportion corresponding to a possible formula, and that this proportion is independent of changes (within certain limits) of the conditions of separation. The evidence for the existence of salt hydrates

[1] *Z. anorg. Chem.* 1893, 3, 267.

[2] Another question is how far we can have double (polymerized) solvent molecules, each attached to the ion only by a single covalency : this will be discussed later (Excessive Hydration, p. 198).

is invariably of this kind : we cannot, as will be shown later,[1] determine the degree of hydration in solution, and we commonly assume that if a solid hydrate of a particular formula separates, this hydrate also exists as a molecule (or as the ions of a molecule) in solution. The same applies to the compounds with ammonia which separate from the solution of a salt in liquid ammonia, or are formed by the absorption of ammonia gas. Again, we have numerous double salts, undoubtedly forming solid phases of definite formula, which nevertheless give no indication of their existence in solution. How far are we justified in assuming that such compounds have any existence as single molecules—that all the constituent atoms are held together by covalencies or electrovalencies ? If we could be sure of it, our task would be considerably simplified. We should know that we had to frame our rules so as to include the constitution of all substances which can be obtained in the solid state with a definite composition expressible by a formula : we should have to find places in our scheme for all the molecules of water in every known hydrated salt. On the other hand we should have to abandon all ideas of a covalency limit, and to admit that many atoms can, under certain apparently quite erratic conditions, expand their valency groups to an almost indefinite extent. But it seems very doubtful whether such a conclusion is justified. We know from X-ray measurements that the crystal unit often contains two or more molecules : in many instances there is no probability that these molecules can combine chemically ; they are packed together in the crystal owing to the operation of forces altogether subordinate to those which unite the atoms in a molecule, these being no doubt due to the weak external fields which surround every atom. If the crystal structure is destroyed by fusion or solution, these molecules separate again. No one would maintain that structural chemistry ought to be able to provide valency links between such molecules—for example, between the two benzene molecules in the crystal unit of solid benzene. But if similar molecules can be held together in the crystal in this way without chemical linkage, why not also dissimilar molecules ? It seems quite possible that when a substance separates from a solvent, the crystal unit may contain one or more molecules of the solvent along with a molecule of the solute, without there being any closer union among these molecules than there is between those of benzene in the crystal unit of solid benzene.

[1] See p. 190.

This view is supported by the existence of hydrates of substances which can scarcely be supposed to be capable of forming a chemical union with the water. Crystalline hydrates have been shown to be formed not only by the halogen derivatives of the paraffins, such as methyl and ethyl chlorides, bromides, and iodides, methylene and ethylene chlorides, and chloroform,[1] but also by methane itself,[2] and even—most conclusive of all—by the inert gases.[3] Most of these contain 6 molecules of water to one of solute. Their melting-points usually lie near 0°, and when the solute is a gas their dissociation pressures are high, and they are only formed under pressure. The hydrates of the inert gases have the following dissociation pressures at 0° : xenon 1·15 atmospheres, krypton 14·5, argon 98·5. It is very difficult to believe that these are real chemical compounds ; it seems much more probable that the components are held together only by the crystalline forces : the open structure of ice no doubt facilitates the production of such aggregates.

Werner certainly thought that water molecules could exist in this form in a crystal. He definitely assigns a position of co-ordination (which we should call covalency) to some of the water molecules in certain hydrates, whilst he assumes that others have no part in the molecular structure. He often took pains to get experimental evidence of this difference of function, by showing that one part of the water could be removed much more easily than the rest, or without such changes in the molecule as further dehydration produced. Biltz has expressed the same view with respect to ammonia. Some compounds are known with enormous numbers (over twenty) of molecules of water or ammonia of crystallization in the formula. We must either suppose that the ordinary rules of covalency maxima, which apply to the great majority of compounds, break down completely in a few cases, or that molecules can coexist in stoichiometric proportions in the solid phase which are not attached to one another by definite links. There is indeed an alternative way of explaining these exceptional substances, which is available when they are compounds with associated solvents, such as water or ammonia ; and that is to suppose that the solvent molecules are not each separately attached to the central atom,

[1] de Forcrand, *C. R.* 1880, **90**, 1491 : 1888, **106**, 1357 : Villard, *Ann. Chim.* 1897 [7] **11**, 377.

[2] de Forcrand, *C. R.* 1902, **135**, 959.

[3] Id., ibid., 1925, **181**, 15.

but are joined to one another in sets of two or more. The undoubted occurrence in water of polymerized molecules, such as H_4O_2, having the structure $H–O–H\leftarrow O\langle^{H}_{H}$, in which the oxygen can still act as a donor, and the possibility (though there is less evidence of this) of a similar polymerization of ammonia, make this suggestion not impossible. The occurrence of double water molecules in hydrated salts was accepted by Werner, and is supported by the fact that in a large proportion of the salts which contain an excessive number of water molecules, this number is 8 or 12.[1] But this explanation cannot be used to overcome the similar difficulty which arises with a large number of double salts. While many of these undoubtedly form complex ions, sometimes of great stability (e. g. ferrocyanides, argenticyanides, &c.), there are many others which give no evidence of their existence except in the solid state; and we may well imagine that in some the components do not actually combine (in the sense of forming valencies), but that all that happens is that the two kinds of molecules pack together into the crystal more easily than either kind separately. This would account for the existence of such salts as $K_{15}TaF_{20}$, which, if it is formulated as a true complex salt $K_{15}[TaF_{20}]$, involves the assumption of a covalency of twenty for tantalum (normal maximum eight), but which may really consist of, say, one molecule of $K_3[TaF_8]$ and twelve of KF, forming separate molecules but a single crystal unit. Similar considerations apply to better known types of double salts, such as the alums $M'M'''(SO_4)_2$, $12H_2O$, which cannot be shown to have any existence outside the solid state.

It seems therefore that we have to bear in mind the possibility that the formula of a solid, where it cannot be confirmed by the properties of the substance in the dissolved or vapour state, may not represent a single molecule, but a crystalline aggregate of separate molecules. This inevitably introduces an element of uncertainty into any discussion of the structure of such compounds, which the X-ray analysis of crystals has not yet removed, although we may hope that it will ultimately do so. We may however provisionally assume that such complications are rare, and that in the majority of solvated compounds each solvent molecule is attached separately to some atom in the solute. We may begin by considering the case of hydrated salts.

[1] See below, p. 199.

HYDRATION OF SALTS

Since we know that salts are in general ionized even in the solid state, each water molecule must be assumed to be attached by means of a co-ordinate link either to the positive or to the negative ion. It is important to observe that a water molecule can be co-ordinated to another atom in two ways—either by the oxygen of the water acting as a donor, or by the hydrogen acting as an acceptor :

$$X{\leftarrow}O\begin{matrix}H\\H\end{matrix} \quad \text{or} \quad X{\rightarrow}H{-}O{-}H.$$

The general evidence indicates that, other things being equal, the oxygen is more likely to form the link than the hydrogen : it is more powerful as a donor than hydrogen as an acceptor. But the electrical condition of the ion X will have an important and possibly a deciding influence. As we have seen, the formation of a co-ordinate link must give something of a positive charge to the donor, and something of a negative charge to the acceptor, since the two electrons which previously belonged to the donor alone are now shared between it and the acceptor. In consequence, the atom is more likely to act as a donor when it is negatively charged, and as an acceptor when it is positively charged, for in this way the electrostatic equilibrium tends to be restored. This means that cations will act as acceptors and form co-ordinate links with the oxygen of the water, while anions will attach themselves to the hydrogen :

$$X^+ \longrightarrow \left[X{\leftarrow}O\begin{matrix}H\\H\end{matrix}\right]^+ \quad : \quad A^- \longrightarrow [A{\rightarrow}H{-}O{-}H]^-.$$

There is thus a possibility of the hydration of both cations and anions, but from the greater co-ordinating power of the oxygen in water we should expect cations to hydrate more easily than anions. The presence of an electric charge, especially a positive one, will obviously promote co-ordination, so that we can understand why salts as a class have a stronger tendency to be hydrated than non-polar substances. The limit of the hydration of both kinds of ions is of course fixed by the covalency maximum.

These remarks apply to the hydration of salts both in solution and in the solid state, but the nature of the evidence available for the two classes of phenomena is very different. The hydration of ions in solution has been investigated by means of a great variety of physical properties, such as the density, viscosity, freezing-point, electrical conductivity, electrolytic transport, and

the effect of neutral salts on solubility (' salting out ') and on the activity and catalytic power of hydrogen ion, as well as in other ways. The experimental evidence is thus extensive enough, but it is very indecisive. Any one who examines the voluminous literature [1] of the subject will, I think, conclude that there is good reason to believe that many ions are hydrated in water, and some evidence as to which ions are more hydrated and which less, but that we can form no quantitative idea of the number of water molecules combined in solution with any particular ion. Different methods of investigation often put a series of ions in the same order, but they differ enormously—sometimes by a factor of twenty—as to the absolute magnitude of the hydration. This is no doubt partly due to the uncertainty of the theoretical basis of many of the methods of calculation adopted, but there is a fundamental difficulty in the way of all of them. The free water molecules behave as electrical dipoles, and hence become oriented in the field of an ion. This means that in addition to any molecules which may be chemically united to the ion, there will be a layer of molecules affected by its field, and for many purposes indistinguishable from those which are chemically combined. This applies especially to arguments based on ionic mobility, and on the electrolytic transport of water. The orientation of the dipoles in the neighbourhood of a moving ion will exert a drag upon it and diminish its mobility, and at the same time this will cause a movement of these unattached water molecules in the direction in which the ion is travelling. Further complications in these electrolytic methods of determining hydration have been pointed out by Lindemann,[2] who shows that the direct impact of the ions on the water molecules will have a similar effect, both on the mobility and on the transport, the magnitude of which will depend on the mass of the ion.

The recent developments of the theory of strong electrolytes, due mainly to Debye and Hückel, while of great importance in themselves, do not at present give us much help towards the solution of the problem before us. From the point of view of the general theory of electrolytes, it is essential to determine the relation of the physical properties of the solvent to its influence on the activity and mobility of the ions : it is a relatively unimportant question how far this is due to the actual linkage of the solvent molecules to the ions. As the theory develops further,

[1] For summaries see Dhar, *Z. f. Elektrochem.* 1914, **20**, 57 : Fricke, ibid., 1922, **28**, 161.

[2] *Z. phys. Chem.* 1924, **110**, 394.

especially in its extensions to weaker electrolytes, and to solvents of lower dielectric capacity than water, we may expect the selective effect of the true chemical links to become more prominent.

The evidence for the hydration of salts in solution is thus too indefinite to be of much use to us. For the hydration of salts in the crystalline state the evidence is definite (and extensive) enough, but it needs some care in its interpretation. If we disregard for the moment the possible presence of water molecules which are part of the crystal unit but not of the complex molecule, it is still clear that the amount of combined water in the crystal need not be the same as in solution, and that in fact it will often be less. The powerful electrical forces between the opposite ions in the solid may overcome the attachment of the water molecules, and eliminate some or all of them. The water of crystallization of a salt is not determined solely by the tendency of the individual ions to combine with water, although this must at least be an important factor. While the amount of water combined with an ion in solution will be independent of the other ion present, in the crystal the number of water molecules may be the sum of those combined with the two ions in solution, or a smaller number: and whether it is less, and if so how much less, will depend on both the ions of the salt. Various attempts have been made to attack the problem from the physical side, but their success is inevitably limited. They are necessarily based on spatial considerations, and on the assumption that the forces between the atoms in a molecule are purely electrostatic and obey Coulomb's law, and they cannot (at present) take account of the quantum effects which must largely determine the stability of covalent linkages. They do, however, show clearly the importance of Fajans' theory [1] that the tendency of an ion to form a covalent link (in this case a co-ordinate link with the oxygen or the hydrogen of the water) is greater (1) the larger its charge, (2) the less its size if it is a cation, and (3) the greater its size if it is an anion.

In spite of all these difficulties, the study of the composition of hydrated salts leads to interesting conclusions. A valuable discussion of the subject, with a detailed summary of much of the evidence, has been given by Lembert.[2] There are a certain number of salts with polyatomic ions, in which the water forms part of a recognized co-ordination complex, as in $[Cr(H_2O)_4Cl_2]Cl$ or $K_2[Cr(H_2O)F_5]$. It is evident that in such complexes, which

[1] See p. 104.

[2] *Z. phys. Chem.* 1923, **104**, 101.

are of great stability, the co-ordination is through the oxygen as donor, whether the complex is positive or negative. But setting these aside, it is clear that the degree of hydration depends much more on the cation than on the anion. To take some of the more conspicuous examples, salts of lithium, beryllium, and calcium are nearly always hydrated : those of potassium, caesium, silver, mercury, and ammonium are usually anhydrous. This suggests that the hydration of anions is of comparatively rare occurrence,[1] which, as we have seen, is to be expected from the fact that the oxygen in water has a much stronger tendency to form co-ordinate links than the hydrogen.

We may therefore consider the following points : (1) the hydration of cations, (2) that of anions, (3) the mutual effect of cation and anion in determining the degree of hydration of the solid salt, and (4) the instances of a greater degree of hydration than appears compatible with the covalency rule.

1. *Hydration of Cations*

The first point to notice is that, as Fajans' theory requires, the hydration increases with the electrovalency ; it is weak with univalent metals, stronger with divalent, and stronger still with trivalent : compare, for example, the series CsCl, anhydrous : $BaCl_2$, 1 and 2 H_2O : $LaCl_3$, 6 and 7 H_2O. With the exception of lithium and sodium, all the univalent metals are almost invariably anhydrous in their salts : K, Rb, Cs, Ag, Au′, Tl′. The second point is that in any given periodic group the tendency to hydration is strongest in the lightest members, and diminishes as the atomic number increases : this again is in accordance with Fajans' theory, since the lightest ions are also the smallest. It is always very strong in the first two periods, and overcomes the first-mentioned tendency in the alkali metals lithium and sodium. It is particularly strong in the two metals of the first short period, in spite of the fact that the hydration is here limited to four : lithium salts are more uniformly and on the average more highly hydrated than those of sodium. In the case of beryllium, which is at once small and divalent, the firmness with which the ion adheres to four molecules of water is so great that the amount of water of crystallization in a beryllium compound can be used as evidence of the presence or absence of beryllium ion. Practi-

[1] This of course refers to the crystal : it is possible that anions are hydrated in solution, but that the linkage is not strong enough to resist the action of the cation in the solid.

cally all the simple beryllium salts (chloride, sulphate, perchlorate, &c.) crystallize with four molecules of water, which are often very difficult to remove. The fact that the acetylacetonate and the so-called basic acetate $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$ are anhydrous, strongly supports the other evidence that in these compounds the beryllium is four-covalent, and not ionized. The double potassium sulphate $K_2[Be(SO_4)_2]$ has only two molecules of water: this indicates that it is a true complex salt, and contains no beryllium ion: the two water molecules are no doubt attached to the SO_4 groups, which, as we shall see, can be shown to have a tendency to hydrate. The oxalate, which has the composition BeC_2O_4, $3H_2O$, shows by its behaviour [1] (for example by its great solubility) that it is not a normal salt; it is certainly complex, and should probably be written $Be[Be(C_2O_4)_2]$, $6H_2O$, having four of the water molecules attached to the beryllium ion, and the other two to the oxalate groups, of the hydration of which there is plenty of other evidence.

In the second member of the second group, magnesium, there is a very strong tendency (not quite so strong as with the smaller beryllium ion) for the hydration to proceed to the limit, which is here six.

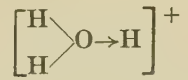
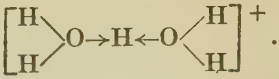
Of the salts of the other polyvalent metals there is little to remark beyond the frequent occurrence of salts with six molecules of water: Werner,[2] in establishing the existence of the co-ordination number six, produced fifty-one examples of such salts. The general diminution of hydration with the heavier metals (owing to increasing ionic size) prevents the covalency of eight from being at all widely represented.

There are two cations which call for special treatment, hydrogen and ammonium (including the substituted ammoniums). There is clear evidence that the hydrogen ion can take up one or two molecules of water, the latter representing its covalency maximum. Practically all the ordinary strong inorganic acids (for example, hydrofluoric, hydrochloric, hydrobromic, hydriodic, nitric, perchloric, sulphuric, selenic) crystallize with water, usually with two molecules (sometimes more) per hydrogen ion. Werner [3] enumerates thirty-three complex halogen acids such as $ZnCl_2,HCl,2H_2O$, that is $[H(H_2O)_2]ZnCl_3$ ('double salts' of simple halogen acids with the halides of Zn, Cu, Cd, Sn, Hg, Sb, Bi, Fe, Au, Ir, Pt, Ag, Te), of which all but four contain at

[1] Sidgwick and Lewis, *J. C. S.* 1926, 1287, 2538.

[2] *Z. anorg. Chem.* 1893, 3, 267. [3] *Neuere Anschauungen*, p. 103.

least $2H_2O$ for every hydrogen ion. The hydrated ion would be written

 and  .

On the Fajans theory the hydrogen ion, from its minute size, should co-ordinate with extreme ease. It is doubtful how far the unsolvated ion can exist in associated solvents at all: it is not improbable that the effect of such solvents in causing the ionization of acids is directly due to their combination with the hydrogen ion. The abnormal mobility of hydrogen ion (which is found in other solvents as well as in water) is no proof that it is not hydrated; it is generally attributed to 'Grotthus conductivity', and one would imagine that this could occur as easily with the solvated ion.

Salts of ammonium and the substituted ammoniums are almost invariably anhydrous. This is to be expected, since in ammonium the nitrogen is covalently saturated, and the hydrogen attached to it can only act as an acceptor under very exceptional circumstances.[1] None of its salts with simple monobasic acids are hydrated, and when we find that the ammonium salt of a dibasic acid is hydrated, we may take this as evidence of the hydration of the anion. This is confirmed, as Lembert has shown, by the fact that the same acids usually form hydrated potassium salts, although of course potassium salts as a rule are anhydrous. He gives the following table to show the extent of the hydration:

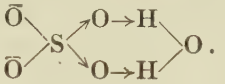
	Ammonium	Potassium
Carbonate .	1	$\frac{3}{2}$, 3
Oxalate . .	1	1
Acid Oxalate .	$\frac{1}{2}$, 1	1, 2
Pentasulphide .	1	(Tetrasulphide 8)
Sulphite . .	$\frac{1}{2}$, 1, $\frac{4}{3}$	1, 2
Thiosulphate .	$\frac{1}{3}$	1
Iodate . . .	$\frac{1}{2}$	? $\frac{1}{2}$
Periodate .	2, 3	4
Dithionate .	$\frac{1}{2}$	0
Orthophosphate .	1	0

2. *Hydration of Anions*

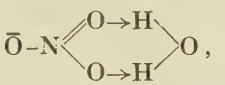
This is on the whole exceptional, but it is well established in certain instances. The most important is that of the sulphate ion. The occurrence of hydrates with an odd number of molecules of water, which as a rule is rare, is almost universal among

[1] See p. 98.

the sulphates. We have Li_2SO_4, $1H_2O$ and Na_2SO_4, $7H_2O$: the divalent metals (Mg, Zn, Cd, Co″, Ni, Mn″, Cr″, V″) give the well-known series of the vitriols, of the general formula $M''SO_4$, $7H_2O$, which may be written $[M(H_2O)_6]$ (SO_4, H_2O).[1] Among the sulphates of the trivalent metals we find those of Al, In, Fe‴, Ce‴, and La with $9H_2O$. A similar example is $CuSO_4$, $5H_2O$, the hydration of the cupric ion being usually limited to four. This tendency of the SO_4 ion to take up water is presumably due to the fact that by so doing (since owing to its negative charge it must attach itself to the hydrogen and not to the oxygen of the water) it can form the stable six-ring



There is some evidence that the nitrate ion also can take up one molecule of water to form a similar six-ring



but the behaviour of nitrates in solution is in many ways abnormal: there are indications that they undergo polymerization.[2]

The oxalate ion is normally hydrated, especially in the double oxalates. It is found generally among organic compounds, whether they are ions or not, that the C=O group takes up a molecule of water readily whenever the next carbon atom is attached to negative groups, and especially when the next group is another carbonyl : this may be unconnected with co-ordination, and due to the conversion of C=O into $C(OH)_2$. Thus glyoxylic acid crystallizes with one molecule of water, oxalic with two, mesoxalic with one, which is retained in its esters, diketosuccinic with two as dihydroxytartaric, and chloral with one, the structures of these hydrates being presumably

$CH(OH)_2{\cdot}CO_2H$: $C(OH)_3{\cdot}C(OH)_3$: $CO_2R{\cdot}C(OH)_2{\cdot}CO_2R$: $CO_2H{\cdot}C(OH)_2{\cdot}C(OH)_2{\cdot}CO_2H$: $CCl_3{\cdot}CH(OH)_2$.

Hydroxyl also appears to take up one molecule of water : all the alkaline hydroxides and thallous hydroxide form monohydrates, often of great stability, though at lower temperatures higher hydrates are also found.

[1] The vitriols are remarkable for giving a series of double salts with the alkali metals and ammonium of the general form M'_2SO_4, $M''SO_4$, $6H_2O$, in which one molecule of water appears to be replaced by one of the alkaline sulphate, a type which it is not easy to explain. [2] See below, p. 198.

Fluorides almost invariably contain water of crystallization, even when the cation is one which is not normally hydrated, as in KF, $2H_2O$ and AgF, 2 and $4H_2O$. This seems to prove that the fluorine ion is itself capable of hydration. The behaviour of fluorine is in many ways difficult to explain. On the one hand it should, according to the Fajans theory, as an anion of small size, pass less readily than the other halogens from the ionized to the covalent state; and the properties of such fluorides as those of aluminium and tin [1] support this view. On the other hand, it has a far greater power than the other halogens of bringing out the highest covalency of an atom, as is shown in H_2F_2, SF_6, OsF_8, &c. This unexpected hydration of fluorine ion may be due to the stability of its co-ordinate link with di-covalent hydrogen, $[F\rightarrow H-O-H]^-$ being analogous to $[F\rightarrow H-F]^-$. There are indications of the hydration of the ions of the other halogens, especially when the cation is unusually large,[2] but they are much less marked than with fluorine.

3. *Mutual Influence of Cation and Anion*

When the hydrated ions separate from the solution, the forces which they exert on one another in the solid will sometimes be sufficient to expel some or all of the combined water molecules. Fajans has suggested [3] that there is a kind of competition between the ions for the water, which is more likely to be retained if the affinity of one ion for it greatly exceeds that of the other. The facts certainly seem to favour this view. Since the chief factor in determining the affinity is the magnitude of the ionic charge, we should, on this hypothesis, expect those salts in which the ions have the same valency to be less often hydrated than those in which the valencies are different. Lembert finds for a large number of soluble salts of the ordinary strong inorganic acids the following statistical results:

Valency cation : anion		Total Salts	Number Hydrated	Per cent. Hydrated
1	1	16	4	25
2	2	8	1	13
1	2	5	5	100
2	1	19	15	79
3	1	14	12	86
4	2	10	9	90

The distinction is very marked.

[1] See p. 88. [2] See below, p. 197. [3] *Naturw.* 1921, **9**, 729.

There are also signs that a large difference in size between the ions tends to promote hydration, quite apart from the requirements of the Fajans deformation theory. This may be one reason why fluorine ion can take up water when it is combined with large univalent (and therefore unhydrated) ions such as potassium or silver. The metallic salts of complex acids are usually highly hydrated unless the cations are exceptionally large. Ephraim has observed with the ammonia compounds [1] (and there are indications of the same tendency with the hydrates) that the salts of very large organic anions, such as those of the aromatic sulphonic acids, have an unusual power of taking up molecules of the solvent. This might be explained by supposing that in such cases the extra molecules are merely attached by the crystalline forces, and not by true covalencies.

There is one fact bearing on the relation between hydration in solution and hydration in the solid state which may be mentioned here. The effect of different salts of the same ionic type (for example, salts of univalent cations and anions) at a given concentration on the vapour pressure of water varies over a large range with the nature of the salt. This can be measured by means of the freezing-points, which are the temperatures at which the solutions in question have the same vapour pressure as ice. The observed differences can scarcely be due to differences in activity or apparent dissociation, if we confine our comparison to strong electrolytes ; but they may well be due to the removal of solvent by combination with the ions of the salt. Hence, though our uncertainty as to the precise laws which hold in comparatively strong solutions prevents us from estimating quantitatively the degree of hydration, we may fairly conclude that a salt which produces a larger depression of the freezing-point at a given concentration is more hydrated than one which produces a smaller depression.

We may compare with one another in this way the salts formed by the alkali metals, silver, and ammonium with the ordinary strong acids such as nitric, sulphuric, perchloric, and the halogen acids, and the alkaline hydroxides, at a concentration of six molecules per cent. (about 3-normal).[2] The depression calculated according to the dilute solution laws for a ' completely dissociated ' binary salt at this concentration is 12·4°. The observed values are somewhat remarkable. All the nitrates

[1] *Ber.* 1918, 51, 644 : 1920, 53, 549 : see also Biltz, *Z. f. Elektrochem.* 1920, 26, 374.

[2] Sidgwick and Ewbank, *J. C. S.* 1924, 125, 2273.

except lithium nitrate, which is the only one of these nitrates hydrated in the solid state, give abnormally small depressions (9·3° to 6·2°): this is evidence of that polymerization of the nitrate ion which has already been mentioned. The nitrites behave in the same way. Setting the salts of these two acids aside, we find that the rest can be divided sharply into two classes —those which form solid hydrates and those which do not. The first class invariably give a larger depression than the second, with the single exception of lithium hydroxide (hydrated), where the difference however is small. The highest value for any non-hydrated salt is 12·3° (potassium iodide): the rest range between this and 10·8°. The lowest value for any hydrated salt other than lithium hydroxide (11·6°) is 13·1° (sodium chloride), and the values rise to 23·0 (lithium iodide). The mean depression at this concentration is for the thirteen salts examined which form no hydrates 11·5°, and for the ten which form hydrates 16·6°. The strong acids hydrochloric, hydrobromic, hydriodic, and perchloric, all of which form solid hydrates, give large depressions— from 16·1° to 23·2°: that given by nitric acid, which also forms a hydrate, but is probably associated to some extent in solution, and possibly partly non-ionized, is 14·3°.

The most surprising result of this comparison is the exact correspondence between the effect of the salt in solution and its power of forming solid hydrates. We should have expected the power of forming solid hydrates to depend not merely on the extent of hydration in solution, but also on the solubility of the hydrate; it appears however that this is not so.

4. *Excessive Hydration*

The great majority of salts do not contain more water than is compatible with the covalency rule, if we allow for the hydration of certain anions, where it is supported by other evidence, as in the vitriols, where we have reason to believe that one of the seven molecules of water is attached to the SO_4, leaving only the normal six for the cation (beryllium does not form a vitriol). But there are a considerable number of salts which contain more water molecules than can be accounted for in this way. We may of course abandon the covalency rule, and admit the existence of co-ordination numbers of eight and twelve throughout the whole table, as Pfeiffer does; but we have so much evidence for the rule that it seems preferable to adopt one of two alterna-

tive hypotheses, either the possibility of double water molecules, or that of crystalline aggregates composed of two or more molecules. It is quite possible that both hypotheses are true in different cases : this certainly was Werner's view. At any rate there is a good deal to be said for the theory of double molecules, which, in view of the undoubted existence of polymerized molecules in water itself, is not intrinsically improbable. The strongest evidence in its favour is the fact that in a great majority of the salts with large numbers of water molecules the number is exactly twice what we should expect on the ordinary theory ; when the necessary allowance is made for the hydration, if any, of the anion we nearly always find either eight or twelve molecules for every cation, just as in ordinary hydrates we commonly find four or six. To secure this result it is sometimes necessary to assign a water molecule to an anion which is not usually hydrated ; but the fact that this assumption, which can be defended on the ground of the exceptional size of the cation, so often reduces the number of molecules remaining to eight or twelve is itself remarkable. Some of the more important examples [1] may be given : first of salts which contain exactly eight or twelve molecules of water to every cation, and then of others which contain these numbers in addition to one water molecule per anion.

Salts with eight molecules of water to each cation :

$[Be, 8H_2O]\ PtCl_6$.
$[Mg, 8H_2O]\ Cl_2 : I_2 : BiCl_5$.
$[Ca, 8H_2O]\ PtCl_6 : O_2$.
$[Sr, 8H_2O]\ (OH)_2 : O_2 : BiCl_5$.

Salts with 12 H_2O to each cation :

$[Mg, 12H_2O]\ Cl_2 : Br_2 : PtCl_6 : SO_4 : (ClO_3)_2$.
$[Ca, 12H_2O]\ Cl_2 : (IO_3)_2 : PtBr_6$.
$[Zn, 12H_2O]\ (ClO_3)_2 : (BrO_3)_2$.
$[Co, 12H_2O]\ Cl_2 : (ClO_3)_2 : S_2O_3 : BiCl_5$.

Examples of salts which may be assumed to have eight or twelve molecules of water to each cation if we assign one H_2O to each anion are :

$[Mg, 8H_2O]\ (Br, H_2O)_2 : (I, H_2O)_2$.
$[Al, 12H_2O]_2\ (SO_4, H_2O)_3$.

It will be noticed that in these salts the cations are di- or trivalent atoms not of very high atomic number and the anions

[1] See Lembert, *l. c.*

predominantly polyatomic: also that beryllium (covalency maximum four) rises to $8H_2O$ but not to 12.

We may conclude that the occurrence of double water molecules attached by single covalencies to the cation is at least probable.

AMMONIA OF CRYSTALLIZATION

The combination of ammonia with salts, like that of water, must be due to co-ordination: but the acceptor properties of the hydrogen are so much weaker in ammonia than in water that we should expect that the linkage would always take place through the nitrogen, and hence that as a rule the cation would be solvated but not the anion. The compounds may be divided according to their mode of production into two classes—those which are formed in aqueous solution, such as the ammines of Werner, and those which are only formed in the absence of water, by the use of gaseous or liquid ammonia. The former must have great stability, since the ammonia competes successfully in their formation with a large excess of water. The strong affinity for ammonia shown in the formation of these ammines is peculiar to certain parts of the periodic table, especially the transition elements in the wider sense (including copper): among these it seems to be strongest (in the first long period) in chromium and cobalt, less strong in copper (cupric), and still less in nickel and iron. The strength of the affinity in these ammines is shown by the fact that the ammonia will remain combined (through the nitrogen) with a negatively charged complex, as in $K[Pt(NH_3)Cl_5]$.

Under more favourable conditions—in the absence of water, especially at low temperatures or in presence of liquid ammonia—addition takes place much more easily; salts will combine with ammonia at least as readily as with water. The stable ammines of Werner, which in presence of water are limited in composition by the ordinary rules of covalency, can in the dry state and with liquid ammonia take up sometimes as many as ten more molecules of the latter.[1] These extra molecules are far more loosely combined: they are easily removed without causing any fundamental change in the compound, and without any great change in the characteristic colour. Their position clearly corresponds to that of the extra water molecules in excessive hydration. The readiness with which they are absorbed increases with the electrovalency of the cation of the ammine.

[1] Ephraim, *Z. anorg. Chem.* **1925, 147, 24.**

The general question of the combination of dry salts with ammonia has been investigated by Biltz and his collaborators in a series of papers [1] dealing especially with the halides of the uni- and divalent metals. These can absorb up to, in many cases, ten or even twelve molecules of ammonia per molecule of salt. The method of investigation was to determine at a series of temperatures down to the freezing-point of ammonia (–78°) the relation between the composition and the dissociation tension: the definiteness of the solid phases was proved by the constancy of the tension with change of composition. From the change of this pressure with temperature Biltz calculates the heat of formation of the compound from the salt and ammonia. The number of ammonia molecules frequently exceeds the covalency limit of the cation (solvation of the anion is not probable), and although with some of these highly solvated compounds the vapour pressure is scarcely less than that of liquid ammonia, this is by no means always the case: thus calcium chloride (limit six) forms $CaCl_2$, $8NH_3$, with a dissociation tension of 100 mm. at $-2°$ (that of liquid ammonia is 100 mm. at $-67°$). Biltz considers that in these highest ammines the later molecules are attached by a different kind of linkage from the earlier, and this is confirmed in the case of the alkaline halides by the marked fall in the heat of addition of ammonia after the first three or four molecules.[2] We may suppose either that the later additions go to form double ammonia molecules, or, since there is much less evidence of the polymerization of ammonia than of that of water, that they form part of the crystal unit but not of the complex molecule.

The general relations between the affinity for ammonia and the charge and size of the cation are much the same as for water: the affinity is greater the greater the charge, and (in any particular group) the smaller the ion, as Fajans' theory requires.

The heat values (Q) calculated by Biltz from the change of dissociation tension with temperature are the partial heats of formation from the simple salt and gaseous ammonia: they include the difference between the lattice energy of the ammoniate

[1] Biltz has collected and summarized the results in *Z. anorg. Chem.* 1923, **130**, 93. For further work see Biltz and others, ibid., 1925, **148**, 145–216.

[2] Another example is beryllium chloride. The covalency limit for beryllium is 4. The compound $BeCl_2,4NH_3$ is extraordinarily stable. Its dissociation tension is 100 mm. at about + 200°, while those of $BeCl_2$, $6NH_3$ and $BeCl_2,12NH_3$ reach 100 mm. at − 49° and − 66° respectively.

and that of the original salt. This question has been discussed by Biltz and Grimm.[1] The lattice energy of a salt is the difference between the energy of the fully ionized vapour and that of the solid salt. For an ammoniate it is equal to the heat (A) evolved when m gram-molecules of ammonia combine with one gram-molecule of the cation in the vapour, together with that (B_m) evolved when the ions recombine and condense to the solid ammoniate. Thus if Q is Biltz's value of the partial heat of formation, and U is the lattice energy of the original salt (which has been calculated by Grimm by the method of Born), then

$$\text{Lattice energy of ammoniate} = A + B_m = U + Q.$$

This gives a more satisfactory method of comparing the affinities than the partial heats of formation of Biltz. From a study of the results so obtained, Biltz and Grimm arrive at the following conclusions :

1. For the same number of molecules of ammonia the lattice energy falls with increasing radius of the cation (Na > Rb, Mg > Ba, Cu′ > Ag) and also of the anion (Cl > I), when the ion has the same number of electrons (eight or eighteen) in the outer (highest quantum) group. (Mercuric salts come out of place in this series: they should fall below cadmium, but are actually nearly as high as zinc ; this may be due to complications caused by the presence of mercurous ions.)

2. A cation with an outer group of 18 or 20 (Pb″) electrons gives a higher value than one in the same period with 8(Cu′ > K, Zn > Ca, Pb > Ba).

3. For cations with the same outer electronic group, the lattice energy for any given number of molecules of ammonia is greater the greater the electrovalency.

4. The differences between the lattice energies with the same cation and the same number of ammonia molecules, but a different halogen, fall with an increase in the ammonia content when the cation has eight outer electrons, but rise when it has eighteen or twenty.

It will be seen that these conclusions are in agreement with the Fajans theory so far as concerns the effect of charge and size of the cation, which alone is solvated. It should, however, be noticed that most of these compounds are known only in the solid state. There is always a possibility that some of them may be compounds not of the ions but of the undissociated (covalent)

[1] *Z. anorg. Chem.* **1925, 145, 63.**

halide. This seems particularly likely with the cuprous and silver halides; they combine with $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, and $3NH_3$, and both the low limit of solvation and the presence of half molecules of ammonia suggest that the halide is polymerized.

Combination with solvents other than water or ammonia—especially with organic substances containing hydroxyl or amino-groups—is frequently observed; it appears to follow the same general lines as the formation of hydrates and ammines, but to diminish in extent as the molecular weight of the solvent increases.

XII

ATOMIC AND MOLECULAR MAGNETISM [1]

IT has been recognized since the time of Oersted and Ampère that magnetism is a property of electricity in motion. Every electric current is surrounded by lines of magnetic force, and every closed circuit is equivalent to a magnet of definite moment. It was suggested by Ampère that a substance like iron owed its magnetic properties to a continuous circulation of electricity in its molecules, and that its magnetization consisted in the orientation of these circuits in the same direction. Now that we know that every atom contains electric charges in rapid motion in closed orbits, the origin of the magnetic properties of matter seems clear.[2] At the same time the relation of the magnetic properties of atoms and molecules to their structure is not yet fully understood. Both on the theoretical and on the practical side there are great difficulties to be overcome. The recent developments in the physical theory of the atom, and especially the introduction of the third quantum number, which has a close relation to the magnetic behaviour, have led to great progress, and have brought the magnetic into relation with the spectroscopic theory ; but it cannot be said that any completely satisfactory theory of atomic and molecular magnetism has yet been proposed. The results which have already been obtained are however of great interest.

As Faraday showed in 1845, substances can be divided as regards their behaviour in a magnetic field into two classes—those which tend to set themselves parallel to the field (paramagnetic) and those which set themselves transversely (diamagnetic). Paramagnetic phenomena are now divided into two sections—those of paramagnetism proper and those of ferromagnetism.

[1] See Stoner, *Magnetism and Atomic Structure*, 1926 : Andrade, *Structure of the Atom*, 3rd Edition, 1927, Chapter XVI : Gerlach, *Materie, Elektrizität, Energie*, Leipzig, 1926, Chapter VIII.

[2] The magnetic field near the nucleus of an atom is of enormous intensity : within the K ring it is even in so small an atom as neon about 10^8 and in uranium about 10^{11} gauss. Macroscopically the most intense permanent fields attainable in the laboratory are between 10^4 and 10^5 gauss, but for periods of the order of 1/100 second a field approaching 10^6 gauss might be produced.

This latter, which is distinguished by the great intensity of the forces concerned and by the occurrence of a lag in the relation between the state of the substance and that of the field (hysteresis and permanent magnetism), is confined to a comparatively small number of metals and a few of their compounds : though in general due to the same cause as paramagnetism it is clearly related to the structure of the solid and is not an atomic property, since certain alloys composed of metals with very small individual susceptibilities (the Heusler bronzes, for example an alloy of 10 per cent. aluminium, 20 per cent. manganese, and 70 per cent. copper) have ferromagnetic properties approaching those of iron. Ferromagnetism, being a special case of paramagnetism, will therefore not be discussed further. Both diamagnetism and paramagnetism are observed with matter in every state of aggregation, and therefore are properties of the atoms or molecules.

The fundamental characteristics of dia- and paramagnetism were established experimentally by P. Curie, who formulated the two laws that diamagnetic susceptibility is independent of temperature, and paramagnetic inversely proportional to the absolute temperature. To both these laws, and especially to the second, there are many exceptions, which is to be expected since the magnetic properties of the atom are certainly affected by its state of combination, which will often vary with the temperature. In the absence of such chemical changes the laws may be presumed to hold.

The foundation of the modern electronic theory of magnetism was laid by Langevin in 1905 : regarding the effects as due to the rotating electrons, he gave a theoretical basis to Curie's laws. Every electronic orbit must have a magnetic moment, but by a suitable arrangement of their axes these may neutralize one another ; the simplest arrangement would be one in which all the orbits occurred in parallel pairs, with the two electrons of each pair revolving in opposite directions. In that case the resulting moment of the atom is zero, but it can be shown that the establishment of an external field will so modify the orbits as to produce a diamagnetic effect, which will be independent of the temperature and state of aggregation of the substance. This diamagnetic effect is common to all matter, whether it is paramagnetic or not.

If the orbital moments do not neutralize one another, the atom is paramagnetic, and this will mask the diamagnetism. In

the presence of an external field such atoms will tend to arrange themselves with their magnetic axes parallel to the field. This orientation will be opposed by the disturbing effect of their thermal agitation, so that unless the field is very powerful it will be very imperfectly accomplished (the magnetization will be far from saturation), and in that case the susceptibility, which is the ratio of the magnetization to the strength of the external field, will be inversely proportional to the absolute temperature.

DIAMAGNETISM

The spectroscopic evidence shows that every ' closed ' group of electrons in an atom—every completed Bohr subgroup, such as the two N_{11} electrons, or the two N_{21} together with the four N_{22}— has no resultant magnetic moment. Hence all simple ions of the effective atomic number of an inert gas, and the inert gases themselves, are diamagnetic. The theory of Langevin enables us to calculate from the diamagnetic susceptibilities the average area of the electronic orbits, and the results are in approximate agreement with those required by the sizes of the atoms as deduced from the X-ray measurement of crystal structure. While we know little about the magnetic moments of the orbits of shared electrons, the facts indicate that these also tend to balance one another, and we may perhaps assume that as a rule (though not always) the two shared orbits forming the covalent link have zero magnetic moment. Hence the majority of compounds of the lighter elements, and in particular most organic compounds, are diamagnetic. Pascal [1] has examined a large number of organic substances, and finds that the molecular diamagnetism is made up additively of a series of values for the component atoms, together with a constitutive term for the type of molecule in question : the property thus varies in much the same way as the molecular volume. Some approach to an explanation of the values of these terms can be made, but the conclusions are not yet sufficiently definite to be worth discussing in detail. The essential outcome is that while molecules containing paramagnetic atoms may or may not be paramagnetic, diamagnetic atoms always combine to give diamagnetic molecules, and to a first approximation the effects are additive.[2]

[1] *Ann. Chim. Phys.* 1910, 19, 1 : 1912, 25, 289 : 1913, 29, 218.

[2] For further information see Stoner, *op. cit.*, Chapters XII and XV.

PARAMAGNETISM

The investigation of paramagnetic substances has already led to important results, and promises to be of the utmost value in elucidating the structures both of atoms and of molecules, although some of the conclusions, especially those dealing with molecules, must be accepted with reserve until the theoretical and the practical sides of the problem have been more fully worked out.

The first question is whether there is a unit of magnetic moment of the atom, as there is a unit of electricity in the electron. On purely experimental grounds Weiss claimed to have discovered such a unit: and this unit, the Weiss magneton, the value of which is $18{\cdot}5 \times 10^{-22}$ ergs/gauss per atom, or 1126 per gram-atom, has been commonly adopted. There is a good deal of evidence in its favour, but it is by no means conclusive, and can scarcely be expected to be so, in view of the large number of magnetons (up to fifty) which have in some cases to be assumed, and the difficulty of accurate measurement. It has not been found possible to derive the Weiss magneton from the known atomic constants. On the other hand Bohr has pointed out that there is a very simple relation between the angular momentum of an electron (on the quantizing of which his theory is founded) and the magnetic moment of its orbit. The angular momentum is the product of the mass of the electron, the angular velocity, and the square of the radius of the (circular) orbit:

$$\mathrm{A} = m \cdot \omega \cdot r^2.$$

On the classical theory of electromagnetism, if we regard the rotating electron (of charge e in electrostatic units) as equivalent to an electric current in a circular conductor, the magnetic moment is

$$\mu = \frac{1}{2} \frac{e \cdot \omega \cdot r^2}{c},$$

where c is the velocity of light.

Hence the two quantities have the simple relation

$$\frac{\mu}{\mathrm{A}} = \frac{1}{2} \frac{e}{m \cdot c}.$$

Now on the Bohr theory (p. 18) the unit of angular momentum is $h/2\pi$ (h = Planck's constant). To this therefore there corresponds a unit of magnetic momentum

$$\mu = \frac{1}{2} \frac{e}{m \cdot c} \cdot \frac{h}{2\pi} = \frac{e}{m \cdot c} \cdot \frac{h}{4\pi}.$$

The value of this unit depends only on the mass and charge of the electron, and is for a single atom $9{\cdot}23 \times 10^{-21}$ or for a gram-atom or gram-molecule 5589 ergs/gauss. This is known as the Bohr magneton : it is remarkable that it is almost exactly five (4·96) times the Weiss magneton.

As will be shown in the next section, we have direct evidence of the existence of the Bohr magneton. The calculation of the moment in Bohr units from the value in Weiss magnetons as ordinarily given is complicated by a fact which will be more fully discussed later. The Weiss magneton numbers are calculated from the susceptibilities on the classical theory, which assumes the angles between the magnetic moments of the atoms and the field to be distributed at random. It has, however, been shown that this is incorrect : only a limited number of values of this angle is possible. Hence we cannot obtain b, the value in Bohr magnetons, simply by dividing p, that in Weiss magnetons, by 4·96 : the factor varies somewhat with the magneton number. The values are given in the following table, which is due to Sommerfeld (Pauli gets values of p about 3 per cent. less).

b (Bohr)	1	2	3	4	5	6	7	8	10
p (Weiss)	8·6	14·1	19·3	24·4	29·5	34·5	39·5	44·5	54·5

The experimental results may be considered under four heads : (1) atomic rays (metallic vapours), (2) paramagnetic gases, (3) monatomic ions, (4) complex ions.

1. *Magnetic Moments of Atomic Rays*

This subject was investigated with the most remarkable results by Stern and Gerlach.[1] The conditions are quite different from those in any other magnetic measurements, in that the beam of metallic vapour used is at so low a pressure that collisions between the atoms (with the consequent disturbance of the orientation) are excluded. Though the experimental difficulties are very great, the principle is simple. A stream of metallic vapour issuing from a hole in a minute electric furnace is passed through two parallel slits so as to reduce it to a flat parallel beam of atoms. This is passed between the poles of a powerful electromagnet so arranged as to give a highly inhomogeneous field, the pole-pieces being close together and one of them wedge-shaped.

[1] Stern, *Z. f. Phys.* 1921, **7**, 249 : Gerlach and Stern, *Ann. d. Phys.* 1924, **74**, 673 : Gerlach, ibid., 1925, **76**, 163. See also Gerlach, *Materie, Elektrizität, Energie*, p. 79. Stoner, *op. cit.*, Chapter IX.

The direction of the beam is along the edge of the wedge, and its greatest width parallel to the base. The beam is then received on a glass plate. The whole apparatus is highly exhausted : the temperature is such that the vapour pressure of the metals is very low (e. g. 1020° for silver), so that the atoms in the beam do not collide with one another, and their velocity can be calculated from the temperature by the kinetic theory of gases. The number of atoms is so small that their trace is frequently not visible on the screen, but it can be made so by a process of ' physical development ' like that used for under-exposed photographic negatives.

The possible results of such an experiment are these. If the atoms have no resultant magnetic moment, the magnetic field will not affect them, and the trace will be a narrow line when the field is on, as it is when it is off (the diamagnetic effect is too small to be perceived). If the atom has a moment, it is equivalent to a small magnet, and in passing through the field will be deflected towards one or other pole according to its orientation, and the more so, the smaller the angle between its axis and the field. On the classical theory we should expect a random distribution of the magnetic axes in the beam to start with, and a resulting broadening of the narrow line produced in the absence of a field into a band thickest in the middle. What is actually observed with silver is not this, but that the beam is split into two. This is only possible if the atomic magnets, when they reach the intense field, are oriented only in two ways—half of them (since the two beams are as far as can be measured equal in intensity) having their magnetic axes parallel, and the other half having them antiparallel, to the field. This is entirely opposed to the older electromagnetic theory, but is in accordance with the quantum theory, which requires that in a magnetic field an atom with unit magnetic moment should take up one or other of these two positions (space quantization). This result will only be reached when, as in these experiments, no collisions between the atoms occur : under higher pressures the orientation will be disturbed by collisions. The time taken for the orientation in Stern and Gerlach's experiments cannot much exceed 10^{-4} seconds ; but this time, though short, is long in comparison with the period of revolution of the valency electron, which is of the order of 10^{-15} seconds.[1]

[1] For a further discussion of the problems raised by this phenomenon see Einstein and Ehrenfest, *Z. f. Phys.* 1922, **11**, 31 : Stoner, *op. cit.*, p. 209.

The experiment further shows that an isolated neutral silver atom has a magnetic moment, and from the separation of the two beams we can calculate its amount. The values obtained are from 5400 to 5700 ergs/gauss per gram-atom, the value for one Bohr magneton being, as we have seen, 5589 ergs/gauss. We thus have direct evidence of the validity of the Bohr magneton.

The application of this method to other metals has led to very interesting results, although the work has not yet been carried very far. Copper and gold, and also sodium and potassium,[1] have like silver a moment of one magneton, all these elements having, in addition to a ' closed ' core, a single electron in an N_{11} orbit. Zinc, cadmium, and mercury, all of which have two valency electrons in N_{11} orbits, have no magnetic moment, nor have tin and lead, which have two N_{11} and two N_{21} orbits. It is clear that with the completion of a Stoner grouplet the magnetic moment cancels out. Thallium ($2 \times 6_{11}$ and $1 \times 6_{21}$) is magnetic, but the separation is only about one-third of that required for one Bohr magneton : this however is to be expected on spectroscopic grounds. Nickel, of which the ' normal ' structure (based on the spectrum) is less certain, is peculiar in that the line is split up by the field into three, some of the atoms being deflected to one side or other to an extent corresponding to two Bohr magnetons, and the rest not being affected. Two different resolved moments for the nickel atoms are therefore possible. Iron, curiously enough, appears to be non-magnetic in the vapour : but its low volatility makes the results uncertain.

A very interesting determination has been made quite recently[2] of the behaviour of atomic hydrogen, which was found to have, like silver and the alkali metals, a moment of one magneton. In order to obtain a trace of the beam, it was received on a glass screen covered by a thin layer of (white) molybdenum trioxide, which was reduced where the hydrogen atoms fell on it to the blue dioxide.

On the whole these experiments, in addition to establishing the Bohr magneton and the space quantization, afford a remarkable confirmation of the conclusions as to the structures of these atoms derived from the spectra and the chemical behaviour.

[1] Taylor, *Phys. Review*, 1926, **28**, 576.
[2] Phipps and Taylor, *Phys. Review*, 1927, **29**, 309.

2. *Paramagnetic Gases*

When we leave these highly rarified vapours, and come to deal with more concentrated forms of matter, the disturbance of the orientation through collisions has to be taken into account. This should be most easily done in gases, which are free from many complications occurring in the liquid and solid states, and it leads directly to Curie's law that (in not too intense fields) the susceptibility is inversely proportional to the absolute temperature. Oxygen, and the gases with 'odd molecules' (molecules containing an odd number of valency electrons), nitric oxide, nitrogen dioxide NO_2, and chlorine dioxide, are paramagnetic. Only two of these have so far been carefully examined—oxygen and nitric oxide. Oxygen was shown by Curie and by Onnes to obey the Curie law from $-113°$ to $+450°$. Its susceptibility and that of nitric oxide were examined with great care by Bauer and Piccard.[1] Their results afford a strong support for the Bohr magneton and the theory of space quantization, the values in Weiss units being for oxygen 14·16 (theory for two Bohr magnetons 14·1), and for nitric oxide 9·20 (theory for one Bohr magneton 8·6). That nitric oxide would be paramagnetic might have been expected, since it has an 'odd molecule': it seems natural that as nitric oxide behaves in many ways like an isolated univalent radical, it should have the same single Bohr magneton as a univalent atom of silver or copper. But it is surprising that oxygen should also be paramagnetic. It has a complete core, and presumably a complete octet of four unshared and four shared electrons, and we should have expected the moments of their orbits to balance one another. Hydrogen, nitrogen, the halogens, ammonia, sulphur dioxide, carbon dioxide, and organic compounds in general (including those which contain oxygen) are diamagnetic, and no explanation has been offered of the exceptional paramagnetism of elementary oxygen.

3. *Simple Paramagnetic Ions*

Extensive investigations have been made of the paramagnetism of ions in solution and in the solid salts, and as far as the monatomic ions are concerned the relation to the atomic structure is at least qualitatively clear. All ions which are composed of complete electronic groups—both those of inert gas number

[1] *J. de Phys.* 1920, 1, 97.

(K^+, Ca^{++}, F^-, I^-, &c.), and the cations of B metals, with an E.A.N. eight units less (Cu^+, Zn^{++}, Cd^{++}, &c.)—are diamagnetic, as are the inert gases themselves : from which it follows that all simple anions are so. Paramagnetism is only found among those ions which contain incomplete electronic groups (transitional elements in the wider sense), and the rare earth metals. For two of the series of such elements, those of the first long period from scandium (21) to copper (29), and the rare earth metals from lanthanum (57) to lutecium (71), this conclusion has been established in detail. Thus scandium (2) (8) (9) (2) gives an ion Sc^{+++}, which is diamagnetic because it has the complete structure (2) (8) (8). The cuprous ion (2) (8) (18) is diamagnetic, while the cupric (2) (8) (17), in which the third quantum group is incomplete, is paramagnetic. The ions La^{+++} and Ce^{++++}, both of which have the E.A.N. (2) (8) (18) (18) (8), are diamagnetic, and so are Lu^{+++} and Hf^{++++}, with the E.A.N. (2) (8) (18) (32) (8); but the ions of the intervening elements, in which the fourth quantum group contains more than 18 and less than 32 electrons, are paramagnetic.

These conclusions are derived from the study of the susceptibilities of salts of these ions in solution and in the solid state. On the quantitative side there is some uncertainty about them owing to the possibility of the values being modified by the formation of covalent linkages : this is indicated by the fact that the solutions and the solids often do not obey Curie's law.[1] Also it must be remembered that the theory of the orientation of atoms, and of the influence of temperature upon it, was worked out for gases, and is less certainly applicable to the ions in a crystal. The values in solution are sometimes dependent to a small extent on the concentration, and appear to be affected also by hydrolysis and by the formation of auto-complexes. But approximate values (at any rate within one Weiss magneton) may be deduced for these ions, and the agreement between the values obtained

[1] Many solids obey Weiss's law $\chi = \frac{C}{T - \Theta}$ where χ is the paramagnetic susceptibility, T the temperature, and Θ a constant. C has the same significance as in Curie's law $\chi = \frac{C}{T}$. Weiss's law may be derived by assuming that there is mutual interaction between the molecules of the solid, of an unknown nature, which is proportional to the intensity of magnetization. (If I is the magnetic moment per unit volume, H the magnetic force, and d the density, the specific susceptibility per unit mass $\chi = I/H.d$.)

in solution, and those given by the crystalline salts, even the oxides [1], is surprisingly good. The values to the nearest Weiss magneton, and the approximate number of Bohr magnetons, are given in the following table, together with the number of electrons in the third quantum group in the ion.

Electrons in 3rd group.	8	9	10	11			12		13		14	15	16	17	18	
Ion	K′, Ca″ Sc‴,Ti⁗	Ti‴	—	V″	Cr‴	Mn⁗	Cr″	Mn‴	Mn″	Fe‴	Fe″	Co″	Ni″	Cu″	Cu′	Zn″
p (Weiss)	0	9	—	9	19	20	24	25	29	29	26	25	16	9	0	0
b (Bohr)	0	1		1	3	3	4	4	5	5	4	4	(2·4)	1	0	0

This shows in the first place that the magnetic moment of the ion depends primarily on the number of electrons and not on the nuclear charge: it is the same for Cr‴, as for Mn⁗, for Cr″ as for Mn‴, and for Mn″ as for Fe‴: this seems to show that it is determined rather by the type of orbit than by the firmness with which the electron is bound. Secondly there is an evident tendency for the moment to increase by one Bohr magneton for each of the first 5 electrons added to the original 8 in the third quantum group, and to fall by 1 for each of the subsequent 5. To this however there are certain exceptions: V″ is 1 instead of 3, Co″ is 4 instead of 3, and Ni″, which should be 2, gives a value between 2 and 3, suggesting an equilibrium between two forms of ion. Of the 10 electrons added to the third group as we pass from one end of this series to the other, 4 go to the 3_{32} grouplet and 6 to the 3_{33}, but there is nothing in the magneton values to indicate that one of these grouplets is completed before the other begins to fill: the curve rather suggests that the two processes go on simultaneously.

The magnetic moments of the ions of the rare earth metals have been determined independently by Cabrera and Stefan Meyer,[2] who used mainly the crystalline hydrated sulphates and the oxides. Their values agree well on the whole, considering the immense difficulty of purifying the materials. The results do not give integral numbers of Bohr units, which may be due partly to incomplete purification: it is also possible that the assumption that these salts obey Curie's law (which has been proved for gadolinium sulphate) is not true for all of them. The

[1] It is assumed that these are polar compounds, or, which comes to the same thing, that the moments of the two shared orbits which constitute a covalency neutralize one another.

[2] *Phys. Z.* 1925, **26**, 51.

values in the following table are the means of those of Cabrera and St. Meyer: approximate Bohr magneton values are given in the last line.

Electrons in 4th group.	18		19		20	21	22	23	24	25
Ion	La'''	Ce''''	Ce'''	Pr''''	Pr'''	Nd'''	Il'''	Sm'''	Eu'''	Gd'''
p (Weiss)	0	0·8	11·4	13·8	17·6	17·8	—	7·5	18·0	40·0
b (Bohr)	0	(0·1)	1·5	1·9	2·7	2·7	—	0·8	2·7	7·1

Electrons in 4th group.	26	27	28	29	30	31	32	
Ion	Tb'''	Dy'''	Ho'''	Er'''	Tu'''	Yb'''	Lu'''	Hf''''
p (Weiss)	46·0	52·6	52·0	46·9	36·5	22·2	0	0
b (Bohr)	8·3	9·6	9·5	8·5	6·4	3·5	0	0

It is thus evident that the ions with complete fourth quantum groups of 18 or 32 electrons are diamagnetic. Between them we have the ions in which the grouplets of $6 \times 4_{43}$ and $8 \times 4_{44}$ are being built up. The fact that the curve falls into two parts, the first with about five elements and the second with nine, suggests that the difference between the energy levels of the grouplets is sufficient for the first to be more or less completed before the second begins to develop, whereas in the first transition series, as we have seen, there is only a single curve, indicating that the 3_{32} and 3_{33} grouplets develop together.[1]

Of the two other transition series (Y 39 to Pd 46, and Hf 72 to Pt 78) only isolated members have been investigated, and though the results seem to be of the same kind as in the first series, the details are not yet clear.

3. *Complex Ions*

The salts of these ions have usually been examined in the solid state, and as a rule only at one temperature: when the temperature has been varied Weiss's law has often been found not to

[1] The atomic moments of the rare earth metals have been correlated satisfactorily with the spectroscopic data by Hund (*Z. f. Phys.* 1925, 33, 855).

hold.[1] This suggests that the substance is really a mixture of two or more forms in equilibrium. It would seem however from the regularity of the results that with many salts the error due to this cause is not large.

With well-established complex ions having a central atom of a transition element, evidence has been adduced by Welo and Baudisch [2] that the paramagnetism depends primarily on the effective atomic number : that when this has the same value as in an inert gas, the complex is diamagnetic, while if it differs from this by n units, the complex has a magnetic moment of n Bohr magnetons. Thus the six-covalent ferricyanides, as $K_3[Fe(CN)_6]$, with an E.A.N. $26+6+3 = 35$, give $p = 10$ (b = ca. 1), while the ferrocyanides, as $K_4[Fe(CN)_6]$ (E.A.N. $26+6+4 = 36$, the atomic number of krypton) are diamagnetic. Replacement of CN groups by NO_2 NH_3, H_2O, &c. (with the change of electrovalency required to preserve the E.A.N.), has no effect. So too the cobaltammines of the well-known series with E.A.N. 36 (from $K_3[CoX_6]$ to $[Co(NH_3)_6]Cl_3$) are all diamagnetic, while the chromammines, with the exactly corresponding formulae, and accordingly an E.A.N. of 33, all give approximately $p = 19$, or $b = 3$. The results are summarized by Stoner in the following table :

Element.	Cr	Ni	Cu	Fe	Fe	Co		Ni
At. No. . . .	24	28	29	26	26	27	—	28
E.A.N. . . .	33	34	35	35	36	36	37	38
p (Weiss) . .	19	13	9	10	0	0	—	16
b (Bohr) approx.	3	2	1	1	0	0	—	2

Thus the nearest Bohr magneton value is in all cases equal to the difference between the E.A.N. of the central atom and 36, the atomic number of krypton. The rule does not appear to hold any longer after the third quantum group of 18 has become firmly established, for the ethylene-diamine compound of zinc chloride $[Zn(en)_3]Cl_2$ (E.A.N. 40) is diamagnetic. It should be noticed that the bichromates and permanganates, in which the central atom has the E.A.N. 26 = (2) (8) (8) ($\underline{4}$, $\underline{4}$), consisting entirely of completed groups and a fully shared octet, are diamagnetic, or at most very weakly paramagnetic.

A few measurements have been made with complex ions of metals of the palladium and platinum series, which show that

[1] Rosenbohm, *Z. phys. Chem.* 1919, **93**, 693.

[2] Welo, *Nature*, 1925, **116**, 359 : Jackson, ibid., 360 : Welo and Baudisch, ibid., 606.

the salts are diamagnetic when the E.A.N. of the central atom is that of xenon or emanation. Thus $[Rh(en)_3]Cl_3$, E.A.N. 54, is diamagnetic, and so are $[Ir(NH_3)_5NO_2]Cl_2$ and $[Pt(NH_3)_4Cl_2]Cl_2$, both of which have the E.A.N. 86. But the four-covalent compounds of platinum and iridium such as $K_2[PtCl_4]$, in all of which the E.A.N. is 84, are diamagnetic likewise.

These results are of unusual interest, and if they can be extended and confirmed will give us a new and powerful means of investigating the constitution of complex molecules. Some examples of this may be given. The constitution of the metallic carbonyls is a very difficult problem. The existence of carbon monoxide is itself surprising, but we have had to recognize that carbon with an E.A.N. of (2) (2, $\underline{2}$, $\underline{2}$) is comparatively stable. It remains to devise a stable attachment of this to a central atom. Though the formulae of the mixed carbonyl compounds tend to show that a CO can replace an NH_3, and so must be attached by a single covalent link, the evidence is not conclusive. If however we can trust the magnetic argument, the question is answered at once. $Ni(CO)_4$ and $Fe(CO)_5$ are both diamagnetic, and so the central atom in both should have an E.A.N. of 36 : for nickel $28+8$, and for iron $26+10$. If so, each carbonyl group must contribute two electrons to the central atom, and the structure is presumably Ni←C=O and Fe←C=O. If this is true, the stability of the compounds is very remarkable : we know no other stable compounds of trivalent carbon with the E.A.N. (2) ($\underline{3}$, $\underline{3}$). Another puzzle is the structure of the ' nitroxyl ' compounds, which contain the NO group in a complex. Now it is found that $Na_2[Fe(CN)_5NO]$ and $[Ru(NH_3)_4Cl(NO)]Br_2$ are diamagnetic. We should infer that the effective atomic numbers of the metals in these complexes are 36 and 54 respectively. This involves the contribution of three electrons by the NO to the central atom :

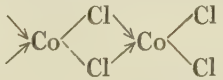
$$Fe\ 26+5+3+2 = 36 : \quad Ru\ 44+8+1+3-2 = 54.$$

This rule relating the magnetism to the E.A.N. raises a question as to the state of the simple ions of the transition elements in solution. As we saw in the last chapter, the natural assumption is that these simple ions, as they are of small size and have a valency greater than 1, are in water practically wholly in the hexahydrated form, as $[Fe(H_2O)_6]^{++}$, &c. ; the readiness with which many of them form stable six-covalent compounds with ammonia supports this view. In that case their real E.A.Ns. in

solution are twelve units higher than those calculated for the simple ions : the ferrous ion, for example, will have an E.A.N. not of 24 (26 −2), but of 36 (26 −2 +12). Hence on the principles which appear to hold for the complex ions discussed above, it should be diamagnetic, whereas it actually has a moment of four Bohr magnetons. The agreement between the values obtained in solution and those given by the crystalline salts (many of which are anhydrous, and which include the chlorides) is also difficult to explain, as it is hard to see how in the solids, even if they are not ionized but covalent, the metallic atom can form as many as six-covalent links. It is, however, worth pointing out that if we assume that in solution these ions form not the hexahydrates but the tetrahydrates, a considerable number of them obey approximately the rule of Welo and Baudisch. The following table gives (1) the ionic symbol, (2) the E.A.N. of the tetrahydrated ion, (3) the difference between this and the atomic number of krypton, and (4) the observed number of Bohr magnetons.

Ion	Cr'''	Mn''''	Mn'''	Cr''	Mn''	Fe'''	Fe''	Co''	Ni''	Cu''
E.A.N. ($4H_2O$)	29	29	30	30	31	31	32	33	34	35
36 — E.A.N.	7	7	6	6	5	5	4	3	2	1
b obs.	3	3	4	4	5	5	ca. 4	4	2–3	1

The results agree with the rule fairly closely (with the exception of cobalt) for the ions from Mn'' to Cu'' : in fact on this hypothesis the moment should fall from 5 for Mn'' and Fe''' by steps of 1 to 1 for Cu'', which as we have seen is what the whole curve for the simple ions leads us to expect. The earlier members of the series do not fall into line : the magneton values fall as we go backwards from Mn'' instead of continuing to rise ; but of course we have no evidence from the behaviour of the complex ions as to whether Welo's rule holds when the difference between the E.A.N. and the inert gas number is greater than three. The coincidence among the later members of the series may be merely accidental, but it is worth noticing, especially as a covalency of four is quite possible in the solid salts, though it is difficult to see how one of six could arise. Such a structure as



is not improbable in view of the great stability of 4-covalent compounds in general. An X-ray examination of these crystals would be of interest.

It will be seen that the magnetic properties of atoms and molecules show promise of becoming of the utmost importance. The theory, although it has made great progress in the last few years, is by no means complete, and many of its conclusions cannot yet be regarded as definitely established. It is only recently that the magnetism of electronic orbits has been seriously attacked from the physical side, and the extension of the theory to shared orbits has not yet even begun. The experimental work also offers peculiar difficulties, and the data are still comparatively scanty. But the magnetic properties afford a new and independent means of attack on the problem of molecular structure, and one which has the advantage of being applicable to non-volatile substances in the dissolved and solid states, whereas the spectroscopic method breaks down under such conditions owing to the broadening of the lines. There is scarcely any branch of the inquiry which seems more likely than the magnetic to lead to important developments during the next few years.

XIII

STEREOCHEMICAL RELATIONS

WE have next to consider the evidence bearing on the arrangement in space of the groups covalently linked to an atom, and the relation of this to the nature of the atom and the number of the attached groups.

The simplest assumptions are that four groups will be arranged at the points of a tetrahedron, six at those of an octahedron, and eight at those of a cube. These may be called the tetrahedral, octahedral, and cubic arrangements respectively, and correspond to the orientation on the Bohr theory of the grouplets of four, six, and eight electrons: they are also of course supported to a very considerable extent by the stereochemical evidence. At the same time a plane distribution is not impossible, and there is evidence of its occurrence with certain 4-covalent atoms.

With carbon van't Hoff and Le Bel independently suggested in 1874 that the four attached groups do not lie in a plane, and van't Hoff proposed the tetrahedral arrangement which has never since been disputed. The deduction from this theory, that the four groups attached to two doubly linked carbon atoms in a compound of the type abC=Cab must lie in a plane, was made at the same time by van't Hoff, and has held its ground likewise. All the later developments of the stereochemistry of carbon are nothing more in principle than experimental proofs of deductions from van't Hoff's original idea.

Compounds showing optical activity due to the arrangement of groups round a nitrogen atom [1] were first [2] obtained in 1899 by Pope and Peachey [3] when they resolved a salt of benzyl-phenyl-allyl-methyl-ammonium. In 1908 Meisenheimer [4] showed that methyl-ethyl-aniline oxide could be separated into its active

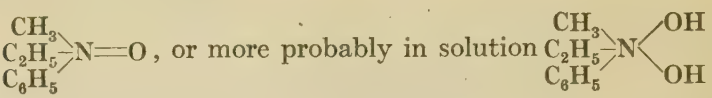
[1] The possibility of a tetrahedral distribution in an ammonium ion was suggested in 1878 by van 't Hoff (*Ansichten über die org. Chemie*, p. 80).

[2] Le Bel in 1891 (*C. R.* **112**, 724) claimed to have obtained a solution of a methyl-ethyl-propyl-isobutyl-ammonium salt of small rotation by allowing a mould to grow in it. Marckwald (*Ber.* 1899, **32**, 560) could not repeat this, but Le Bel (*C. R.* 1899, **129**, 548) published a confirmation of his earlier experiments.

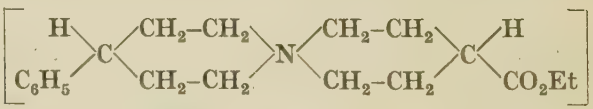
[3] *J. C. S.* **75**, 1127.

[4] *Ber.* 1908, **41**, 3966.

components by means of its *d*-bromocamphor-sulphonate, and that the liberated base,



(as these compounds were then formulated), retained its optical activity. Whichever be the correct formula, this proves that a nitrogen atom attached to only four different groups (not five) can be optically active, whereas if it has two similar alkyl groups we know that the activity disappears. Meisenheimer concluded that four of the groups attached to an ammonium nitrogen atom are arranged tetrahedrally, and that the fifth (ionized) group occupies no fixed position. This is of course in complete agreement with our modern views of the nature of polar and non-polar linkages. Although Meisenheimer's evidence is strong, and the development of the theory of electrovalency has further strengthened it, it is not absolutely conclusive: the possibility of the five groups attached to a nitrogen atom occupying the points of a square pyramid (as suggested by Bischoff in 1890, and accepted by H. O. Jones in 1905) is not definitely excluded. The final proof of the tetrahedral structure was given by Mills and Warren.[1] They prepared 4-phenyl-4′-carbethoxy-bispiperidinium-1 : 1′-spiran bromide

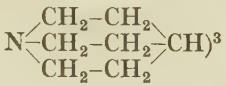


and resolved it through the bromocamphor-sulphonate: this gave an optically active bromide ([M] $\pm$50·7°). The original compound is formed with a readiness which indicates that there can be little strain in the two rings. It can easily be seen on a model that if the two rings are attached to the base of a square pyramid, the molecule will have a plane of symmetry, whereas if they are attached to the points of a tetrahedron it will not. Thus the pyramidal structure is shown to be incorrect, and the tetrahedral is confirmed. This is precisely what we should expect on the electronic theory, since the neutral carbon atom and the positively charged nitrogen have the same number of electrons.

The distribution of the groups in compounds of trivalent nitro-

[1] *J. C. S.* 1925, 127, 2507.

gen of the type N*abc* is still a matter of some doubt. The electronic theory does not at present help us to answer this question. If the three groups attached to the nitrogen have the same relative positions as three of the four in an ammonium ion, the molecule will obviously be asymmetric ; but even then it is not improbable that the antimers may change into one another so easily in the absence of a fourth group that the compound will be permanently racemic. It is also conceivable that when the fourth position is unoccupied the orbits may be so far distorted that the three lie in the same plane with the nitrogen atom. On the theoretical side therefore the question is open.[1] All attempts to prepare optically active compounds of the type N*abc* have failed. Meisenheimer has recently [2] reviewed the subject, and come to the conclusion that singly linked trivalent nitrogen (except possibly when it forms part of a polycyclic system, as in



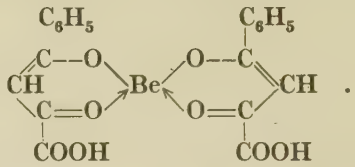
cannot give rise to optical activity. He considers that the groups do not lie in a plane, but that the molecule changes continuously from one asymmetric form to the other, and that this process is only arrested when the fourth covalency is occupied.

Where two of the covalencies of trivalent nitrogen are attached to the same atom, it can be shown that the third is not in the same plane with the other two. This conclusion was made very probable by the explanation which it gave of the isomerism of the oximes,[4] and later of the diazo-compounds (Hantzsch) ; it was definitely proved by the work of Mills and Bain [5] for the oximes, and subsequently by the same authors [6] for the hydrazones and semicarbazones.

The tetrahedral symmetry is therefore established for carbon and 4-covalent nitrogen. Of the other elements in the first short period, it has been proved to occur with beryllium and boron, and almost certainly with oxygen. With beryllium its occurrence was made probable by the work of Lowry and Burgess,[7] who showed that beryllium benzoyl camphor (in which

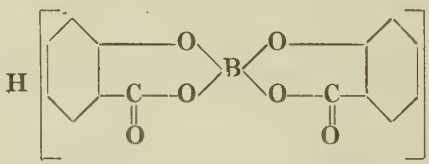
[1] For a further discussion of this point see below under sulphur (p. 228).
[2] Meisenheimer, Angermann, Finn and Vieweg, *Ber.* 1924, **57**, 1744.
[3] See *Ann.* 1920, **420**, 190.
[4] Hantzsch and Werner, *Ber.* 1890, **23**, 11.
[5] *J. C. S.* 1910, **97**, 1866.
[6] Ibid., 1914, **105**, 64.
[7] *J. C. S.* 1924, **125**, 2081.

the metallic atom forms part of two unsymmetrical rings) undergoes considerable mutarotation in solution. As in this compound the mobile hydrogen atom of the benzoyl camphor is replaced, it is difficult to see how the mutarotation can be due to anything but a racemization of the groups attached to the beryllium atom: in which case the arrangement round this atom must be tetrahedral. A more definite proof was provided by Mills and Gotts,[1] who resolved the beryllium compound of benzoylpyruvic acid



The alcoholic solution of the brucine salt, when quite pure, showed a mutarotation from $[\alpha]$ 39·9° to $[\alpha]$ 13·1° in three hours. By adding the brucine salt to a solution of dimethylamine hydrochloride in alcohol, nearly the whole of the alkaloid was precipitated as the hydrochloride, and the filtrate, measured at once, had a rotation α = +1·13°, which sank in fifteen minutes to −0·1°.

With boron the same conclusion was established by Boeseken and Meulenhoff,[2] who prepared the strychnine salt of borosalicylic acid,



and by recrystallization from water obtained a dextrorotatory fraction ($[\alpha]$ +22·6°). As strychnine and its salicylate are both laevorotatory, this showed that the boron complex was dextrorotatory. Both the free acid and its salts racemized very rapidly, and they could not be obtained in the active form. That the same distribution occurs with 4-covalent oxygen is indicated by the work of Morgan and Bragg[3] on the basic acetate of beryllium $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$. They showed that the molecule of this compound (which is not ionized) is a regular tetrahedron, with an oxygen atom at the centre, and four beryllium atoms

[1] *J. C. S.*, 1926, 3121.
[2] *Proc. K. Akad. Wetensch.* 1924, 27, 174: *J. C. S.* Abstr. 1924, i. 776.
[3] *Proc. Roy. Soc.* 1923, 104, 437.

at the corners. The same structure[1] must also occur in the analogous zinc and zirconyl compounds $Zn_4O(O{\cdot}CO{\cdot}CH_3)_6$ and $(ZrO)_4O(O{\cdot}CO{\cdot}CH_3)_6$. It might be argued that this only shows that the four valencies of the oxygen atom can assume this arrangement under strain; but the remarkable stability of the compound, and the great readiness with which it is formed, indicate that there is no considerable strain in the molecule.

Thus we have good evidence that the atoms of five of the seven valent elements of the first short period have, in the 4-covalent state, the four groups arranged tetrahedrally round them; and we may take it that this is the only arrangement possible for elements whose maximum covalency is four.

With the heavier elements, whose maximum covalency is six or eight, we have definite proof that in the 6-covalent form (nothing is known at present about the spatial distribution of eight covalencies) many of them have the six groups placed at the points of an octahedron. This has been proved by the test of optical activity for chromium, cobalt, iron, rhodium, iridium, arsenic, and aluminium.

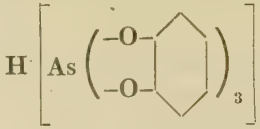
In 1911 Werner was able to resolve the 6-co-ordinated cobalt compounds with two and three chelate groups, such as $[CoCl(NH_3)(en)_2]X_2$[2], $[CoClNO_2(en)_2]X$[3] and $[Co(en)_3]X_3$[4] into their optical antimers, and thus established his octahedral theory for this element; the final proof that the activity was not due to some conceivable rearrangement of the organic groups was given when he resolved[5] the complex compound

$$\left[Co\left(\begin{matrix} OH \\ OH \end{matrix}\right)Co(NH_3)_4\right)_3 \right] Br_6,$$

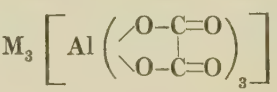
which contains no carbon at all. He further prepared optically active compounds containing 'asymmetric atoms' of chromium,[6] iron,[7] and rhodium.[8] The resolution of an asymmetric compound of iridium, $K_3[Ir(C_2O_4)_3]$, was effected by Delépine.[9] Recently Rosenheim and Plato[10] have obtained an

[1] The structure will be discussed in Vol. II under Beryllium.
[2] *Ber.* 1911, 44, 1887 (en = ethylene diamine).
[3] Ibid., 2445, 3272, 3279.
[4] *Ber.* 1912, 45, 121.
[5] *Ber.* 1914, 47, 3087.
[6] $[Cr(en)_2Cl_2]$ X, *Ber.* 1911, 44, 3132 : $K_3[Cr(C_2O_4)_3]$, ibid., 45, 3061.
[7] Ibid., 1912, 45, 433.
[8] Ibid., 45, 1228.
[9] *Bull. Soc. Chim.* 1917 [4], 21, 157.
[10] *Ber.* 1925, 58, 2000.

optically active compound of 6-covalent arsenic. The cinchonine salt of tricatechol-arsenic acid



on crystallization from alcohol separated entirely as the salt of the *l*-acid (owing presumably to continuous racemization in solution). From this the free acid and its potassium and barium salts were obtained, which showed high activity. The conditions of racemization of these compounds are obscure; the salts appear to be unaffected by hot water or alkaline solutions, but are at once racemized by traces of acid. This work is of peculiar interest because, as we shall see, arsenic has been shown to have a tetrahedral structure in its 4-covalent compounds: it is so far the only element which has been proved to give optically active compounds both of the tetrahedral and of the octahedral type. Aluminium has been found [1] to give an optically active 6-covalent compound in its trioxalato-salt



The strychnine salt on extraction with cold water leaves behind a less soluble fraction from which ammonium iodide precipitates the strychnine as iodide, while the ammonium salt

$$(NH_4)_3[Al(C_2O_4)_3]$$

remains in solution. This gives a rotation $[M]_D+81{\cdot}2°$, which falls to half its value at the ordinary temperature in forty-five hours.

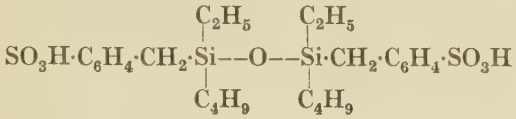
We may thus take it as proved that the octahedral arrangement is that of the 6-covalent compounds of many elements, and may assume with some probability that it is that of 6-covalent compounds in general.

Among the 4-covalent compounds of elements heavier than fluorine (i. e. with a maximum covalency of six or more) we find a more complicated situation. Two different spatial arrangements occur: the tetrahedral, giving optical activity under the same conditions as with carbon or nitrogen, and a plane arrangement, which cannot give optical activity at all, but leads to the

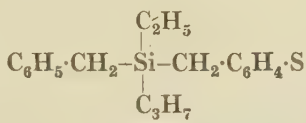
[1] Wahl, *Ber.* 1927, **60**, 399.

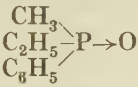
production of two chemically isomeric forms of any compound of the type Xa_2b_2, which is of course impossible with a tetrahedral disposition of the groups.

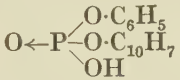
Tetrahedral symmetry—optical activity with four different groups—has been established for silicon, phosphorus, sulphur, selenium, arsenic, copper, zinc, and probably tin. The silicon compounds [1] were (1) the substituted silicoethers



and (2) substituted silicanes



Though the success of the resolution can scarcely be doubted, the rotation was exceedingly feeble. With phosphorus Meisenheimer [2] has shown that the spatial relations of the amine oxides are repeated in the phosphine oxides: methyl-ethyl-phenyl-phosphine oxide  was resolved through the bromocamphor-sulphonate, and was found to have a molecular rotation of about 40° in water. This is the only type of phosphorus compound in which optical activity has been definitely proved. Kipping [3] has obtained indications that the unsymmetrical diaryl hydrogen phosphates, such as

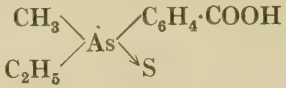


exist in active forms, but this cannot be said to have been established.

With arsenic numerous unsuccessful attempts have been made to resolve both the arsonium salts and the arsine oxides. Burrows and Turner [4] claimed that they had obtained active *d*-phenyl-naphthyl-benzyl-arsonium iodide, but the maximum rotation they obtained was only 0·1° in a 2-dm. tube. Mills and Raper [5]

[1] Kipping, *J. C. S.* 1907, **91**, 209, 717 : 1908, **93**, 457.
[2] Meisenheimer and Lichtenstadt, *Ber.* 1911, **44**, 356.
[3] Kipping and Challenger, *J. C. S.* 1911, **99**, 626.
[4] *J. C. S.* 1921, **119**, 426. [5] *J. C. S.* 1925, **127**, 2479.

finally obtained definite proof by the resolution of *p*-carboxyphenyl-methyl-ethyl-arsine sulphide



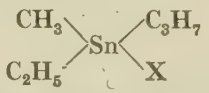
This substance was chosen because the sulphide has none of the basic properties of the oxide, and the arsenic atom is thus protected from disturbance in the course of the separation, the necessary salt formation being performed by the remote carboxyl group. The acid was resolved through the brucine and morphine salts, and had a rotation of about [M] 55°. It showed no tendency to racemize.

The resolution of optically active 4-covalent cupric and zinc compounds was effected by Mills and Gotts,[1] as with beryllium, by means of the benzoyl-pyruvic acid derivative. The alkaloidal salts in both cases showed very rapid mutarotation (the half-life period was about five minutes), but the activity was sufficiently evident.

Thus the 4-covalent compounds of silicon, phosphorus, arsenic, copper, and zinc show essentially the same relations as those of carbon and nitrogen, although the smaller stability of the substances makes their investigation less easy.

The only other elements after the first short period which have been shown to act as centres of asymmetry in molecules in which they have a covalency of less than six, are sulphur, selenium, and tin. The behaviour of these elements raises a question of great interest.

In 1900 Pope and Peachey[2] prepared the bromocamphorsulphonate of methyl-ethyl-propyl tin,

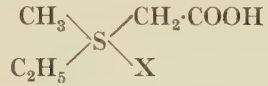


The salt that crystallized from water was the *d*-base-*d*-acid compound, which indicated in a freshly prepared solution a cationic activity of about [M]$_{\sim}$+45° ; but the mother liquor on evaporation gave a further crop of the same salt (and no *l*-base-*d*-acid salt) owing presumably to continuous racemization during evaporation.[3] The iodide obtained from this salt had a rotation of [α] +23° as a maximum, but racemized very easily. The experi-

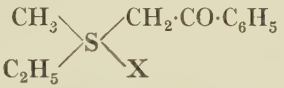
[1] *J. C. S.* 1926, 3121. [2] *Proc. C. S.* 16, 42, 116.

[3] Compare the similar behaviour of the 6-covalent arsenic compound, p. 224.

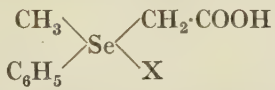
ments were not continued, mainly on account of the physiological properties of the substances, but the results seem beyond doubt ; for it was shown that the bromocamphor salt when first dissolved in water had an activity of $+318°$ and gave with potassium iodide an active iodide : that after the solution had been heated on the water bath for two hours its activity fell to $+275°$, and the iodide which it now formed was inactive : and finally that from this heated solution there crystallized out on evaporation the original dextro-dextro salt. The same authors in the same year [1] resolved the camphor-sulphonate and the bromocamphor-sulphonate of methyl-ethyl-thetine



by recrystallization from alcohol and from acetone, and precipitated the sulphur base as its platinichloride $B_2[PtCl_6]$, which they showed to have an activity in water of about 30°. At the same time Smiles [2] resolved the sulphonium salt



in the same way. This was repeated and confirmed by Pope and Neville,[3] who showed that the picrate of Smiles's base had an activity of about $\pm 35°$; the activity persisted in the platinichloride. In the same paper Pope and Neville describe the resolution of the analogous selenitine

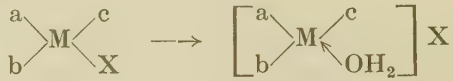


by the same methods. The platinichloride has a molecular rotation of $\pm 55°$. For some unknown reason both the sulphur and the selenium compounds, while they retain their activity in the form of camphor- and bromocamphor-sulphonates, picrates, and chloroplatinates, lose it at once if they are converted into the double mercuric halides $B[HgCl_3]$ and $B[HgI_3]$.

These results are very remarkable, because in every case the active compounds have one of their four groups attached by an ionized link. They are all of the type $[MR_1R_2R_3]X$, where R_1 R_2 R_3 are organic radicals, and X is the anion of a strong acid such as hydriodic, bromocamphor-sulphonic, or chloroplatinic.

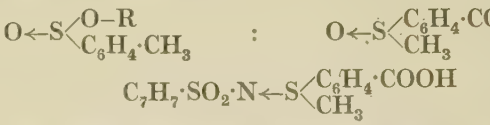
[1] *J. C. S.* 1900, 77, 1072. [2] Ibid., 1174.
[3] Ibid., 1902, 81, 1557.

There is no doubt that they can be ionized without the activity disappearing. This would seem to show that the groups occupying three points of a tetrahedron can retain their positions even when the fourth point is unoccupied. It was suggested by Meisenheimer [1] that these complex ions never exist as such: that in the absence of water the molecules are covalent, and that their ionization by water is due to the direct replacement of the anion by a co-ordinated water molecule:



so that the central atom is never really trivalent.[2]

The existence of asymmetric molecules with only three groups attached to the central atom has been definitely proved in the last two years by the work of Kenyon and Phillips, who have resolved sulphinic esters,[3] unsymmetrical sulphoxides,[4] and the sulphilimines [5] of Mann and Pope



all of which must owe their activity to the arrangement of the three groups round the sulphur atom. This work is of interest in the first place as giving independent evidence of the existence of these co-ordinate links. It is clear that on the older formulae, in which the sulphoxide, for example, is written with a doubly linked oxygen $\begin{matrix} R \\ R_1 \end{matrix}\!\!>\!S=O$, asymmetry is impossible, since two of the valencies of the sulphur are attached to one single atom: the three groups must lie in the same plane with the sulphur. The only possible formula for an asymmetric molecule is one in which the sulphur is joined to the oxygen by a single link, and since the stability of the compound shows that the octet of the oxygen must be complete, this link must be formed of two electrons derived from the sulphur. This conclusion is also supported by Sugden's measurement of the parachor of the sulphinate in question.

We are thus compelled to admit that in these compounds

[1] *Ber.* 1924, 57, B. 1744.
[2] See farther, p. 229, note.
[3] Phillips, *J. C. S.* 1925, 127, 2552.
[4] Harrison, Kenyon, and Phillips, ibid., 1926, 2079.
[5] Clarke, Kenyon, and Phillips, ibid., 1927, 188.

the three groups can retain their places in spite of the fact that the fourth point of the tetrahedron is unoccupied. The same is presumably true of selenium, and probably of tin, in the compounds described above. There is no objection to be raised to this on physical grounds ; the only difficulty is to explain why the trivalent nitrogen atom, which has precisely the same electronic arrangement, should have been found to be incapable of giving active forms. Phillips points out that in every instance where a tri-covalent atom has been found to act as a centre of asymmetry, that atom is positively charged, either as a cation (in $[R_1R_2R_3M]X$, where M = S, Se, or Sn) or as a donor (in $R_1R_2S{\rightarrow}O$ and $R_1R_2S{\rightarrow}NR$) ; and he suggests that it is the presence of this charge which prevents the racemization of the molecule. This conclusion can scarcely be accepted without further evidence. The proof that activity is impossible in the absence of such a charge rests on the single case of nitrogen : no other trivalent element has been investigated in sufficient detail. The physical arguments are not definite enough to be of value in the present state of our knowledge, and the question can only be settled by further experimental work.[1]

So far it appears that elements with a maximum covalency higher than four, when they form tri- or quadri-covalent compounds, have the groups arranged tetrahedrally. But this is not always so. Some elements form compounds in which the four groups certainly lie in a plane. The first examples of this were recognized by Werner[2] in the 4-co-ordinated platinous com-

[1] Meisenheimer's suggestion, that the central atoms in the salts $[R_3S]X$, $[R_3Se]X$, and $[R_3Sn]X$ are really 4-covalent, replacing a covalent X group by a co-ordinated H_2O when they ionize in water, is thus seen to be unnecessary to explain the activity of the sulphur and presumably of the selenium compounds. It is not supported by the properties of the sulphonium compounds, which are those of true salts ; they are non-volatile, and like ammonium salts are precipitated from alcoholic solution by ether in a non-solvated form. It is not so certain that Meisenheimer's view is wrong in the case of tin. The alkyl-tin salts, like stannic chloride itself, may well assume a covalent form in the absence of ionizing solvents, and only become ionized by solvation. This distinction between the two classes of compounds is supported by the difference in the structure of the central atoms. Whereas the sulphur and selenium ions, as formulated without hydration, contain complete octets (2, $\underline{3}$, $\underline{3}$), as does a trivalent nitrogen atom, the tin compound can only complete its octet either by recombination with its anion, or by co-ordination with a molecule of solvent :

$[R_3Sn]^+$: $\underline{3}$, $\underline{3}$. $[R_3SnX]^\circ$, $[R_3Sn(OH_2)]^+$: $\underline{4}$, $\underline{4}$.

[2] *Z. anorg. Chem.* 1893, **3**, 310.

pounds of the type $[Pt(NH_3)_2Cl_2]$: these all occur in two chemically and physically different forms, which is only possible if the four groups lie in the same plane with the central atom, admitting

of a cis $\begin{matrix} Cl \\ Cl–Pt–NH_3 \\ NH_3 \end{matrix}$ and a trans $\begin{matrix} Cl \\ NH_3–Pt–NH_3 \\ Cl \end{matrix}$

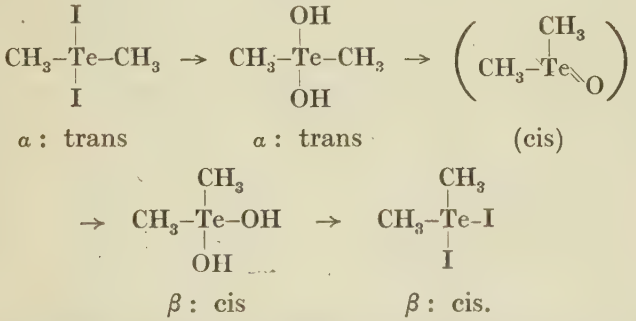
arrangement. This isomerism is widely distributed among the 4-covalent platinous derivatives; it is found not only in a variety of un-ionized compounds of the diammine series, but also in complex ions both positive and negative : it occurs in the pyridine derivatives of the tetrammine series $[Pt(NH_3)_2py_2]Cl_2$,[1] and also in the salts $K_2[PtCl_2(NH_2SO_3)_2]$.[2] Werner's interpretation was recently challenged by Reihlen,[3] but it has been vindicated by Hantzsch.[4] The isomeric compounds of the diammine type are usually very insoluble, and their molecular weights were not determined by Werner. Reihlen found that the chlorides $[Pt(NH_3)_2Cl_2]$ were soluble in liquid ammonia, and that in this solvent, while Werner's cis compound had the normal molecular weight, his trans compound was bimolecular. Reihlen concluded that the isomerism was solely due to the polymerization, and that no inference could be drawn as to the spatial distribution of the four groups. Hantzsch found that the corresponding pyridine compounds $[PtCl_2py_2]$ (which exhibit the same isomerism) are soluble in phenol, and showed that they both give normal molecular weights by the cryoscopic method in this solvent. Werner's view that the isomerism is due to the arrangement of the four groups round the platinum, and that these must therefore lie in the same plane with the metal, is thus fully confirmed.

Similar relations are stated to hold with cobalt,[5] but the evidence is inconclusive. The cobaltous halides on treatment in the dry state with ammonia yield diammines $Co(hal)_2$, $2NH_3$, and these can be obtained in two differently coloured forms ; for example the chloride in the α-form is pink and in the β-form blue. The blue form on heating goes over into the pink. No other definite differences could be established, as neither form will dissolve in any solvent without decomposition. Until further

[1] Jörgensen, *J. pr. Chem.* 1886 [2] **33**, 510.
[2] Kirmreuther, *Ber.* 1911, **44**, 3115.
[3] Reihlen and Nestle, *Ann.* 1926, **447**, 211.
[4] *Ber.* 1926, **59**, 2761.
[5] Biltz and Fetkenheuer, *Z. anorg. Chem.* 1914, **89**, 97.

evidence is forthcoming, no conclusions can be drawn from these facts as to the nature of the isomerism.[1]

The only element other than platinum which has been proved to give 4-covalent compounds in which all the groups lie in a plane is tellurium. Vernon [2] has shown that the product $Te(CH_3)_2I_2$ obtained from tellurium and methyl iodide occurs in two forms. The original (α) iodide yields in solution a hydroxide, from which it can be re-formed. But if this hydroxide is heated it is converted (presumably through the oxide $(CH_3)_2Te{=}O$) into an isomer, which differs in chemical and physical properties from the original hydroxide, and on treatment with hydriodic acid forms a different (β) iodide. The isomeric bromides and chlorides were also prepared. The molecular weights of both forms of all three halides were determined (by the boiling-point in acetone, and by the freezing-point in benzene and nitrobenzene), and were found to be normal. It is remarkable that the two forms differ greatly in their physiological effects, the α being far more powerful than the β. This isomerism must be due, like that of the platinous compounds, to the four groups lying in a plane, and the method of transformation indicates that the first product is a trans compound, whose hydroxide can lose water only by going over to the cis (as fumaric acid forms maleic anhydride), from which the second (β = cis) iodide is produced :



The evidence therefore indicates that a four-covalent atom, if it belongs to the first short period, and is thus exerting its maxi-

[1] The numerous alternative formulae possible for such compounds when their molecular weights are unknown are illustrated by the platinum compound $[Pt(NH_3)_2Cl_2]$, of which, in addition to the two monomeric isomers described above, there exist two dimeric forms $[Pt(NH_3)_4]$ $[PtCl_4]$ and $[Pt(NH_3)_3Cl]$ $[Pt(NH_3)Cl_3]$, and two trimeric forms $[Pt(NH_3)_3Cl]_2[PtCl_4]$ and $[Pt(NH_3)_4]$ $[Pt(NH_3)Cl_3]_2$, the structures of all of which are quite well established.

[2] *J. C. S.* 1920, 117, 86, 889 : 1921, 119, 105, 687.

mum covalency, always has the four attached groups arranged tetrahedrally. If it is an element of a higher atomic number, and accordingly has a maximum covalency of six or more, it may still have this arrangement, and is found to do so in most of the instances which have been examined (Si, P, S, Cu, Zn, As, Se, Sn). But a plane arrangement is also possible, and has been established for the two elements tellurium and platinum. It is unfortunate that the number of elements for which this property has been determined is too small for it to be possible for any general conclusions to be drawn as to its relation to atomic structure ; we do not even know whether the same element can have a tetrahedral arrangement in some of its 4-covalent compounds and a plane in others. It may, however, be pointed out that there is a certain structural resemblance between the two atoms which are known to give the plane configuration. They both have a similar but unusual relation to the 6-covalent atoms of the same elements. The normal relation between the 4- and 6-covalent states of the same atom is that both have the same core, but the latter has four more shared electrons. Thus

Si in $[SiF_6]^{--}$: 22_6 = (2) (8) $\underline{6}$, $\underline{6}$.
Si in SiF_4 : 18_4 = (2) (8) $\underline{4}$, $\underline{4}$.

So the arsenic in the active 6-covalent catechol derivative is 40_6 = (28) $\underline{6}$, $\underline{6}$, and in the active 4-covalent sulphide 36_4 = (28) $\underline{4}$, $\underline{4}$. But in both the tellurium and the platinum compounds the 4-covalent atom with the plane configuration, while it necessarily has four less shared electrons than the 6-covalent, has two more unshared (i. e. there is a change of valency in the classical sense) :

Te in TeF_6 : 58_6 = (28) (18) $\underline{6}$, $\underline{6}$.
Te in $Te(CH_3)_2I_2$: 56_4 = (28) (18) 2, $\underline{4}$, $\underline{4}$.
Pt in $[Pt(NH_3)_2Cl_4]$: 86_6 = (60) (14) $\underline{6}$, $\underline{6}$.
Pt in $[Pt(NH_3)_2Cl_2]$: 84_4 = (60) (14) 2, $\underline{4}$, $\underline{4}$.

Whether the two unshared electrons should appear as part of the valency group, or as an example of the ' inert pair ' (N_{11} grouplet), may be disputed ; but their occurrence in the only two classes of compounds for which the plane configuration has been established is remarkable.

XIV

CHELATE RINGS

THE formation of chelate compounds has already been briefly discussed (Ch. VII and VIII) and their importance in determining the maximum covalency of elements pointed out (Ch. IX). In this chapter we shall consider the relation of their stability to the number and nature of the atoms which compose them, and the links by which they are held together.

The possibility of the formation of closed rings by means of co-ordinate links was first suggested by Tschugaeff in 1907 [1] in the case of the metallic compounds of biuret and similar substances. The idea was developed immediately afterwards by Werner,[2] who applied it to a very large number of compounds, including on the one hand the metallic derivatives of such substances as acetylacetone, and on the other the compounds formed by dyes with mordants. In recent years the same ideas have been applied extensively by Morgan and his collaborators [3]; the word chelate was suggested by Morgan [4] to describe atomic groups which are capable of forming rings with metallic (or other) atoms by means of one or two co-ordinate links.

The methods by which the presence of chelate rings can be detected have already been discussed. With the metallic compounds they consist mainly in showing that the metal is not present as a simple ion, and either that the whole molecule is covalent, or, if it is ionized, that the metallic atom is part of a complex ion which includes the chelate group. In complex ions of type A (below, p. 239) a divalent anion such as the carbonate ion is proved to be covalently attached to the central atom by the fact that the complex gives no reactions of that anion, and is proved to form a ring because it must occupy two places on the central atom in order to make up the co-ordination number. The evidence for the closing of a chelate ring through hydrogen depends on the fact that if this hydrogen atom forms a second (co-ordinate) link with another atom in the same molecule, it cannot do so with an atom in another molecule: it cannot promote association. Since the hydrogen atom in question usually forms part of a hydroxyl group, so that the compound would

[1] *J. pr. Chem.* **75**, 153: *Ber.* **40**, 1973, 3498. [2] *Ber.* 1908, **41**, 1062.
[3] *J. C. S.* from 1913 onwards. [4] Ibid., 1920, **117**, 1457.

normally be highly associated, the change of properties resulting from chelation is considerable. On comparison with otherwise similar but non-chelate compounds the substance is found to be more volatile, more soluble in non-associated and less in associated solvents.[1]

A rather unexpected but valuable source of information as to the possible types of chelate rings is provided by the study of the structure of mordant dyes.[2] That the action of mordants is due to the formation of co-ordinated ring compounds with the metal was first pointed out by Werner,[3] who not only showed that many mordant dyes had structures analogous to those of compounds known to form such rings, but also proved that cloth mordanted with chromium or iron salts was actually dyed by immersion in a solution of a β-diketone or a β-ketonic ester, such as acetylacetone or acetoacetic ester. These substances are of course colourless, but the dyeing of the cloth is shown by the change of colour of the iron or chromium mordant itself. More recently Morgan and his collaborators have prepared and analysed a large number of chelate metallic compounds of a variety of mordant dyes (especially of the alizarine class), and have established their constitution. It may thus be taken as proved that the power of dyeing cloth mordanted with metallic salts is an indication that the dye is capable of forming chelate rings. This enables us to extend our knowledge of the possible forms of chelate ring by examining the structure of these dyes.

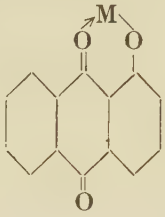
In any catalogue of dyes there will be found a large number (for example, some 160 are enumerated in Schultz, *Farbstofftabellen*, 1914) of dyes of established constitution which can be mordanted with salts of polyvalent metals. Of these all but some half dozen contain a replaceable hydrogen atom and a donor atom so disposed as to be able to form a ring of either six or five atoms (124 of the former and 33 of the latter in Schultz's list) connected to the aromatic ring in the ortho-position. The great majority of these rings are of types already known on other evidence to occur in chelate compounds. For example, the most important type of chelate ring from every point of view is the

[1] See Chapter VIII, p. 147.

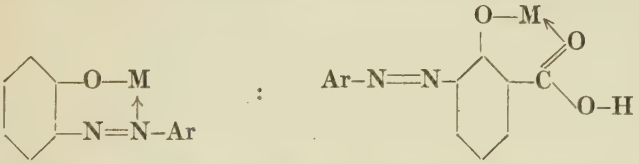
[2] This term is used to describe those dyes which only adhere to the fibre after it has been treated with a salt of a polyvalent metal such as chromium iron or aluminium. There is another method of mordanting, by treating the cloth with tannin and an antimony compound ; but the mechanism of this process is quite different, and so are the types of dyes to which it is applicable.

[3] *loc. cit.*

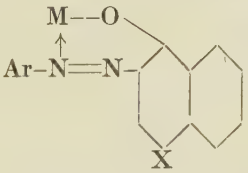
6-ring containing two conjugate double links. This occurs in nearly all the chelate compounds mentioned in the preceding chapters. Among mordant dyes we have an immense number of compounds of this type. All the alizarine dyes are substitution products of 1-hydroxy-anthraquinone and hence can form this ring : [1]



in which M represents one equivalent of the metal of the mordant. Among the azo-dyes it is an established principle that two classes are always mordant dyes : (1) those in which the first component (the diazotized amine) has an ortho-hydroxy-group ; and (2) those in which the second component is a salicylic acid derivative. Both of these classes can give rings of this type :



It is possible to obtain the same ultimate structure as in (1) by introducing the ortho-hydroxy-group in the second component instead of the first, for example, by coupling a simple diazo-compound with a β-naphthol or a para-substituted α-naphthol, and the product is always found to be a mordant dye.



When the azo-group does not couple in the ortho-position to the hydroxyl, the compound is not a mordant dye.

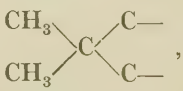
Chelate rings differ from the ordinary isocyclic and heterocyclic rings of organic chemistry in containing co-ordinate links,

[1] It is assumed that the link between any two carbon atoms in a benzene nucleus can be regarded as a double link.

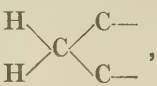
and this form of link, as we have seen, is always a source of instability, since the products of its rupture are in general more stable than those formed by breaking a normal covalency. This comparative instability is shown by the fact that while normal rings with any number of atoms from three to eighteen are known, chelate rings never contain less than four and very rarely more than six. This limitation of size is evidently due to the effect of strain, to which the co-ordinate link renders these rings peculiarly sensitive. We may therefore consider briefly the strain theory of Baeyer and its later developments.

STRAIN THEORY OF BAEYER

This theory was founded on the simple assumption that the angle between two of the valencies of an atom has a ' natural ' value determined by the atomic model, and that any departure of the angle from this value produces a corresponding strain or instability in the molecule. For carbon on the tetrahedral model of van 't Hoff the natural angle (the angle between the lines joining the centre of a regular tetrahedron to two of its angular points) is 109° 28′. Ingold,[1] as the result of work carried out in Thorpe's laboratory, proposed a modification of this theory. He pointed out that the tetrahedron can only be regarded as regular when the carbon atom is joined to four atoms of the same size, and that therefore the angle between the two valencies forming part of the ring will vary according to the nature of the two other atoms attached to the carbon ; if these are also carbon atoms, as in



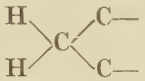
we may assume that the tetrahedron is regular, and that Baeyer's value of the angle holds good, but if they are smaller atoms, as in



the angle will be larger. To calculate its value, Ingold adopts a model formed by taking four spheres of volumes proportional to the atomic volumes of the attached atoms, and arranging them so as to be in contact with one another and with an enclosed

[1] *J. C. S.* 1921, **119**, 305. A similar view was suggested qualitatively by Mamlock (*Stereochemie*, Leipzig, 1907, pp. 99, 100), and even foreshadowed by Wislicenus (*Räumliche Anordnung der Atome*, Leipzig, 1888, pp. 75–6).

sphere. This gives an irregular tetrahedron, and the angle between any pair of valencies is that subtended at the centre of the enclosed sphere by the line joining the centres of the two attached spheres in question. In this way he calculates that the angle between the two carbon valencies in the group



is 115° 18′. Much evidence has been brought forward by Thorpe, Ingold, and others which strongly supports this hypothesis as a qualitative theory. But its quantitative value is much less certain. The difficulty which faces us as soon as we attempt any refinements on Baeyer's original idea is that of giving a definite meaning to the word strain. We may take it that the distortion of the orbits of the shared electrons from their natural positions produces a resisting force, and that this force—or the distortion which causes it—tends to weaken the attachment of the atoms to one another. We may also take it that the distortion, the resisting force, and the consequent weakness all increase together ; but beyond this we know nothing of the laws which relate them to one another. Moreover the ' natural angle ' of no strain must be determined by the geometry of the electronic system. If we adopt Ingold's view that the nature of the attached groups alters the size of the angles, this is itself a distortion of the orbits, and must set up a resisting force of some kind ; this means that the distortion will be shared among the angles concerned, but in what proportions we do not know. We are therefore not justified in assuming either that Ingold's simple calculation of the angles from the volume relationships of the attached groups is correct, or that the resulting angles are ' strainless '.

Hence while the existence and the importance of strain are undoubted, any theory can only be a rough approximation to the facts, and we cannot hope at present to reach quantitative accuracy. So long as this is recognized, the theory of strain is of considerable value, and it is important to compare its predictions with the experimental facts ; and for this comparison the chelate rings are peculiarly suitable, owing to the simplicity of their rupture, which does not involve any extensive intramolecular rearrangement.

On the simple Baeyer theory we have certain fundamental values of the angles, based on the regular tetrahedron, which may

be assumed to hold not only for carbon, but also for all atoms of the first short period, and all other atoms in compounds in which they show the tetrahedral type of symmetry (see last chapter). For the simple angle $C\begin{smallmatrix}C\\C\end{smallmatrix}$ the value is $2\tan^{-1}\sqrt{2} = 109° 28'$. For the angle $C\ll\begin{smallmatrix}C\\C\end{smallmatrix}$, if we assume that the two doubly linked tetrahedra have an edge in common, it is $180° - \tan^{-1}\sqrt{2} = 125° 16'$. From these values we can calculate the strain (that is, the deflection from the natural angle) in rings of various sizes, both with and without double links. The results are given below: the strain is assumed to be equally distributed among the atoms of the ring, and is counted as positive when the polygonal angle is less than the natural (when the strain is ' inwards '). It is also assumed that no atom forms more than one double link.

Strain per Atom of Ring.

No. of atoms in ring.	*Number of double links.* 0	1	2	3
3	+49° 28′	+60° 0′	—	—
4	+19° 28′	+27° 22′	+35° 16′	—
5	+ 1° 28′	+ 7° 47′	+14° 6′	—
6	−10° 32′	− 5° 16′	± 0	+ 5° 16′

It has long been recognized that when the strain is in this sense negative, the theory no longer holds, because it assumes that the ring lies in a plane. This gives the maximum angle of the polygon, and therefore the least strain when the strain is positive; but when it is negative, an appropriate departure from the plane configuration will remove it entirely. At the same time it is evident from the behaviour of normal organic rings that negative strain is not negligible or at least connotes difficulty of formation, for rings of more than six atoms are comparatively rare. We can therefore see that, provided the strain is shared equally among the members of the ring, the most stable forms of ring should be a saturated 5-ring and a 6-ring with two double links. This is fully confirmed by experiment.

When an atom has a covalency of less than four, as in divalent oxygen or trivalent nitrogen, the most reasonable assumption is that the angle between the valencies remains the same as when the full covalency is exerted.

We have so far considered only atoms with a tetrahedral arrangement of the attached groups. With the co-ordinated hydrogen atom the simplest assumption would seem to be that

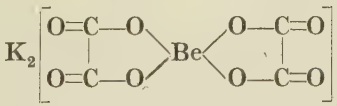
the angle between the two valencies is 180°, but we have at present no means of discovering whether this is actually so. With 6-covalent atoms the natural angle between two adjacent valencies is 90°, and the same is true of those 4-covalent atoms in which the attached groups have been shown to lie in a plane. As we have seen, this disposition has only been established for two elements, tellurium and platinum ; it is, however, possible that others of the heavier elements may be able in their 4-covalent compounds to assume this form, and of this there is some evidence, though it is not conclusive.[1]

The size of the component atoms must also have an effect. In the simple theory it is assumed that they are all of the same size, and this is very nearly true of those important constituents of chelate rings carbon, nitrogen, and oxygen, of which the diameters according to the X-ray data are about 1·5, 1·3, and 1·3 $\times 10^{-8}$ cms. respectively. The heavier atoms which form part of many chelate rings are of course larger, but the ease with which the ring is formed when the metallic atom is replaced by hydrogen suggests that the size is not of great importance.[2]

TYPES OF CHELATE RINGS

We can classify the various kinds of chelate rings in two ways—either by the nature of the links which hold the ring together, or by the number of atoms which it contains. In respect to the nature of the links, we can distinguish three types.

Type A. Rings which, strictly speaking, are formed entirely of normal (not co-ordinate) covalencies, but only in virtue of the central atom having taken up one or more electrons. The ring is formed by the replacement by the metal of two hydrogen atoms in a dibasic acid (including such weakly acidic substances as catechol) : examples are the sulphato- and oxalato-compounds of Werner, such as



They may be called co-ordination compounds of ions, as when they dissociate they normally form ions, the beryllium salt above,

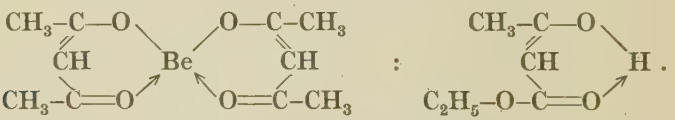
[1] See below, p. 244.

[2] If we can assume that the natural angle is 180° for hydrogen and 90° for the heavier atoms, this would of course tend to compensate for the difference in size.

for example, giving beryllium ions and oxalate ions. Of the four electrons required to enable the beryllium atom to replace four hydrogen atoms, two are taken from the potassium, so that the complex is a divalent negative ion. The value of the electrovalency in such compounds varies widely, being in fact equal to the number of hydrogen atoms replaced minus the valency of the central atom. Thus boron needs one electron to form a dichelate compound of this type, while aluminium needs three in the trioxalato-compounds, and so on.

Chelate rings of this type are remarkably stable, as is shown by the occurrence among them of 4-rings which are almost, and of 7- and even 8-rings which are quite, unknown among other classes of chelate compounds.[1] Two reasons may be given for this. The ring is held together entirely by normal covalencies, and so may be said to possess in some degree the stability of the ordinary rings of organic chemistry. Further, although it has the possibility of dissociating into the simpler ions (e. g. a complex oxalate into the metallic ion and the oxalate ion), the tendency of these to recombine is strengthened by the positive charge on the acceptor (the metallic ion) and the negative charge on the donor.

Type B. Rings with one definite co-ordinate link, in which the metallic (or hydrogen) atom is joined to the ring on one side by a normal and on the other by a co-ordinate link, as in beryllium acetylacetone or the enolic form of acetoacetic ester



This is the largest and most important class. With atoms of which the covalency maximum is twice the valency, one chelate ring is formed for each valency, and a neutral molecule is produced, in which the central atom has its maximum covalency, as in BeA_2 [2] and AlA_3. Owing to the stability of covalencies of four and six, even with atoms which can reach a higher limit, compounds of this kind occur also with the heavier elements of the second and third periodic groups, as in BaA_2 and LaA_3, though these sometimes tend to increase their covalency by hydration (as in BaA_2, $2H_2O$, in which the barium is 6-covalent)

[1] See pp. 243, 251.

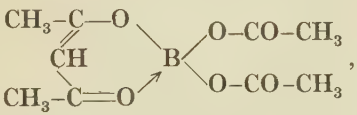
[2] A = radical of diketone.

or by polymerization. When the valency is one more than half the maximum covalency, the latter is reached when all but one of the valencies are occupied with chelate groups; the last valency must then appear as an electrovalency, and we get a salt, as in $[BA_2]X$ and $[SiA_3]X$.

This type of ring is less stable than type A, as is shown by its never containing less than five or more than six atoms. When the co-ordinate link breaks, the primary product must be an open-chain molecule such as $M{-}O{-}C(CH_3){=}CH{-}CO{-}CH_3$, the carbonyl group returning to its normal form, while M remains covalently attached to the oxygen of the hydroxyl group: the covalency of M diminishes by one (it loses its share of a pair of electrons), the process being analogous to the loss of ammonia from a complex ammine. But it is found that another change practically always follows, the remaining normal covalency of the metal being converted into an electrovalency:

$$M\begin{matrix}X\\Y\end{matrix}) \longrightarrow M{-}X{-}Y \longrightarrow M[X{-}Y]$$

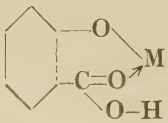
In other words, the covalent compound changes into a salt. It is very rare, at any rate with the more stable types of chelate compounds, to find a substance in which a potentially chelate group is attached only by a single covalency: it is either attached by two to form a ring, or it is ionized. Boron, for example, with a valency of three and a maximum covalency of four, can form compounds of the type of the acetate $B(O{\cdot}CO{\cdot}CH_3)_3$ —non-chelated, tri-covalent—and also of the type of



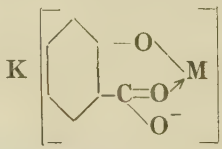
a neutral substance with one chelate ring and two uni-covalent groups. A compound BA_3, in which one of the acetylacetonyl groups was chelated while the other two were merely attached by a normal covalency, would satisfy the covalency rule, but no such compound exists. When the central atom is a metal—especially a highly electropositive metal—this result is to be expected. The metal has a strong tendency to form electrovalencies rather than covalencies, and this tendency can be overcome only when the energy of formation of the normal covalent link is supplemented by that of the co-ordinate link. But it is remarkable that the same thing should occur with an element

like boron, which always forms covalent links in preference to electrovalent.

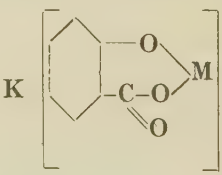
The chelate derivatives of salicylic acid might be referred either to type A or type B. In these compounds, which are very numerous, it has been shown that it is the phenolic and not the carboxylic hydrogen which is replaced, since they are still formed when the hydroxyl of the carboxyl group is replaced by hydrogen (aldehyde) or methoxyl (ester), but not when the phenolic hydrogen is replaced by methyl, in the phenol ether. Thus the salicylic ring can be written as



in which the acid hydrogen is still present. In the salts of this univalent acid we shall then have the ionized form



The compound thus appears as an example of type B. But the salt can equally well be written on type A, the central atom M taking an electron from the K and so replacing the two hydrogen atoms in the salicylic acid :

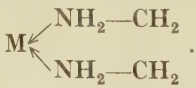


In the present state of our knowledge we cannot decide which of these formulae is correct ; the difference between them is the difference between the two oxygen atoms in the ion of a carboxylic acid $R-C\langle\overset{O}{\underset{O}{}}$; and though as the formula is here written the distinction is quite clear, one oxygen atom sharing two and the other four electrons with the carbon, it is by no means certain that this really represents the structure of the carboxylic ion.[1]

[1] See further, p. 252.

An argument of some force in favour of the second way of writing these compounds is that these complex acids are almost always much stronger than the simple acids from which they are derived; on the other hand the chelate derivatives of salicylic ester cannot be written in this way.

Type C. Rings containing two co-ordinate links, as in the ethylene diamine (' en ') compounds of Werner



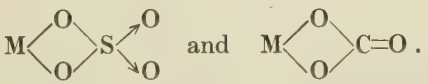
Rings of this type are also formed by β-diketones and similar substances with metallic atoms whose covalency is more than twice their valency, as with the alkali metals.[1] The metallic atom replaces an atom of hydrogen in one molecule of the diketone, and a second molecule is then added without replacement. Rings of this type are as a rule less stable than those of type B, because the whole molecule can break off by the rupture of the two co-ordinate links.

We have now to consider the principal kinds of chelate rings which have been found to occur, and these are most conveniently classified according to the number of atoms in the ring. In order of importance the 6-rings come first, followed by the 5-rings. 4-rings are comparatively scarce, and only occur under special conditions; 7- and 8-rings are entirely limited to type A, and only very few of them are known.

4-RINGS

These are rare, and practically all belong to two peculiar species.

(1). Complex ions containing anions of dibasic acids of the form $\begin{matrix}H{-}O\\H{-}O\end{matrix}\!\!>\!X$, such as the sulphato- and carbonato-compounds of Werner

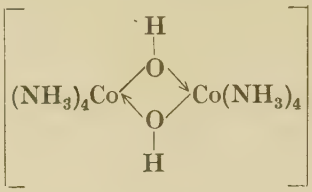


Some of these are remarkably stable, such as $[Co(CO_3)(NH_3)_4]Cl$, from which silver nitrate precipitates only the chlorine, and barium chloride precipitates nothing.

(2). The other established class of 4-rings consists of certain

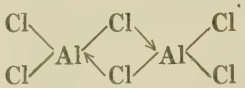
[1] See p. 146.

'polynuclear' co-ordination compounds (i.e. containing more than one metallic atom in the complex), such as

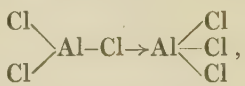


A large number of these are known,[1] some of which have the OH replaced by NH_2. There seems no reason to dispute Werner's formulation of them, and it will be noticed that the two metallic atoms are 6-covalent, so that the natural angle between their valencies is 90°. This reduces the mean strain in the ring to half (from +19° 28′ to +9° 44′).

We have assumed, as Werner does, although the evidence is not conclusive, that a 4-ring of this type exists also in the polymerized covalent halides of the trivalent metals, that Al_2Cl_6 for example is



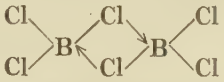
It is evident that the reason why the trihalides of the third periodic group are usually polymerized, while the tetrahalides of the fourth group are usually not, is that the former strive to acquire a complete octet, which the latter already possess. If the ring is not formed, the structure must be



which only completes the octet of one of the two aluminium atoms ; and in that case it is difficult to see why the polymerization does not proceed farther. On the other hand the 4-ring structure would seem to involve too great a strain for a ring with two co-ordinate links, unless we can suppose that an atom which is capable of a covalency of six can have (although as we have seen it does not usually do so) in its 4-covalent compounds a plane distribution of its valencies such as we find in tellurium and platinum. On this assumption the angle between the valencies of the metallic atom is 90°, and the strain is halved, the ring being of the same kind as in the polynuclear cobalt compounds

[1] See Werner, *Neuere Anschauungen*, 1923, pp. 269–91.

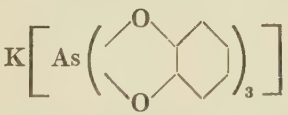
mentioned above. If we extend this idea to the halogen atom as well, the strain vanishes entirely except in the fluorides, since fluorine is the only halogen for which a covalency of six is theoretically impossible : and the fluorides do not polymerize as the other halides do. This hypothesis is rather bold, and is certainly not proved ; but it is supported by one remarkable fact. Boron, being in the first short period, cannot under any circumstances be 6-covalent, and so the natural angle of its valencies must always be the tetrahedral angle of 109° 28′ ; a 4-ring such as



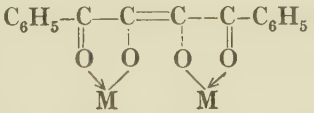
would therefore be impossible, and this may be the reason why boron, which is the only element in the third group incapable of a covalency of six, is also the only element in that group to form trihalides which are not polymerized, and are correspondingly volatile.

5-RINGS

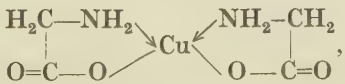
These occur in all three types A, B, and C. *Type A* is especially common in the double oxalates or oxalato-compounds, and in the numerous derivatives of catechol, such as the optically active arsenic compound



Type B. The low boiling-point of catechol itself as compared with its meta and para isomers indicates that it is to a considerable extent chelated. Other examples are the metallic derivatives of the benzoin of phenyl-glyoxal

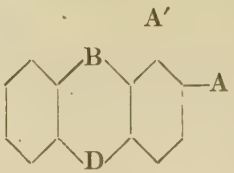


and certain derivatives of glycocoll, especially the copper compound

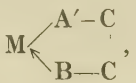


whose properties show it to be covalent. Another series of compounds which must form rings of this type is found among mordant dyes. Nearly all the mordant dyes which cannot form

chelate 6-rings of the kinds described in the next section are of the type

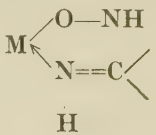


in which B is oxygen (rarely sulphur), D nitrogen (rarely carbon), and A and A′ are hydroxyl (rarely NH_2). We cannot suppose that chelation takes place between B and A (which would give a 6-ring), because compounds in which a second ring is attached to the benzene nucleus in the meta position are almost if not quite unknown, and as all these dyes contain a hydroxyl or NH_2 at A′, it is to be presumed that the chelate ring closes between B and A′, giving a 5-ring of the type

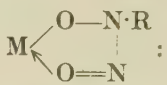


where A′ is nearly always oxygen, and B is also oxygen (or sulphur).

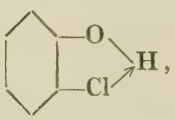
Other 5-rings are found in the hydroxamic acids



according to Werner: in the 'cupferron' compounds



and presumably to some extent in the ortho-halogen-phenols



as is definitely though not very strongly indicated by their boiling-points and solubilities (see p. 148).

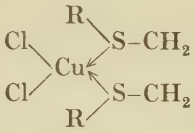
Type C. This includes the numerous co-ordination compounds in which a molecule of ethylene diamine replaces two of ammonia, such as those with which Werner first established the optical activity of molecules of the octahedral type. These compounds

are especially prevalent among the transition elements, as is to be expected from the strong affinity of these elements for ammonia.

A similar ring is formed [1] by the ethers of thioglycol,

$$R{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}R\,,$$

for example with copper.



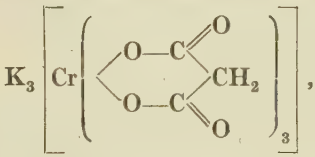
It will be noticed that the majority of chelate 5-rings have no double links, owing to the fact that the reduced 5-ring has the least strain.

6-RINGS

These are by far the most numerous, and the great majority of them belong to one class, that in which there are two conjugate double links

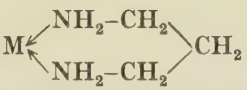
and in consequence on the simple Baeyer theory it is possible to have no strain. Before dealing with this, the most important of all the classes of chelate compounds, we may consider some other kinds of chelate 6-rings, although these are comparatively rare.

Of type A are the malonato-compounds, for example



which has been resolved into its optical antimers. Another group of compounds which essentially belongs to this type occurs in the complex acetates, which will be discussed later.

Of type C are the trimethylene diamine compounds of Werner containing the ring



which are formed by cobalt, nickel, and similar elements. It is remarkable that while 1 : 2 and 1 : 3 diamines react with such

[1] Tschugaeff, *Ber.* 1908, 41, 2222.

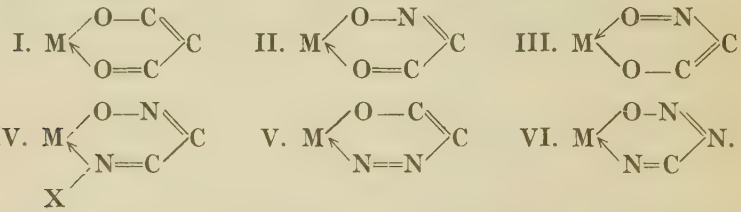
elements with almost equal ease[1] to form 5- and 6-rings respectively, it is impossible to form 7- or 8-rings by the use of 1 : 4 and 1 : 5 diamines. These last give[2] amorphous compounds in which probably a series of metallic atoms are linked in open chains through diamine molecules, as in

$$Ni{\leftarrow}NH_2(CH_2)_4NH_2{\rightarrow}Ni{\leftarrow}NH_2, \text{ \&c.}$$

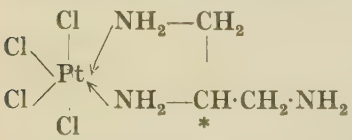
We should expect to find among chelate as we do among normal rings that the stability was less when there were more than six atoms in the ring, but the entire absence of rings with more than six atoms in any chelate compounds except those of type A could hardly have been anticipated.

6-RINGS WITH TWO DOUBLE LINKS

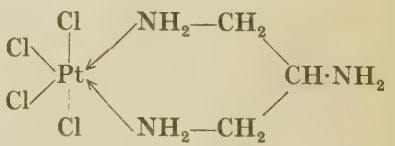
The greater number of known chelate compounds contain 6-rings of type B (with one co-ordinate link), having two double links in the ring. The atoms forming the ring (other than the metal or hydrogen atom) may be carbon, nitrogen, and oxygen ; for obvious reasons the two atoms united to the metal will not be carbon. According to the nature of these atoms we may distinguish at least six classes of rings, of which the more important representatives are enumerated below.



[1] An interesting proof that among saturated rings the five are more stable than the six has recently been given by Mann and Pope (*Nature*, 1927, 119, 351 : Mann, *J. C. S.* 1927, 1224). They prepared the monochelate compound of platinic chloride and $\alpha\beta\gamma$-triaminopropane. According as the ring is formed through the α and β or the α and γ amino-groups it will have five or six members :



α–β : 5-ring.



α–γ : 6-ring.

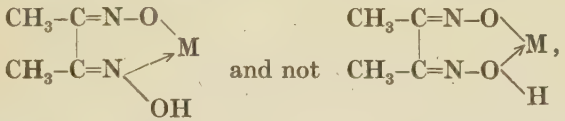
The first of these has a centre of asymmetry in the β-carbon atom (marked with an asterisk) : the second is symmetrical. The product was shown to have the first formula by resolution into its optical antimers. Thus the 5-ring is formed in preference to the 6. [2] Tschugaeff, *Ber.* 1906, 39, 3190.

Class I. β-keto-esters (acetoacetic ester) : β-diketones (acetylacetone) : α-dicarboxylic esters (malonic) : salicylic acid, ester, and aldehyde : 1-hydroxy-naphtho- and anthraquinone : ortho-hydroxy-acetophenone. These are some of the more familiar examples : they have been sufficiently discussed already.

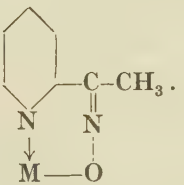
Class II. Ortho-quinone oximes : ortho-nitrophenol : monoximes of α-diketones : oximes of α-ketonic esters.

Class III. Chelate compounds containing this ring are formed by nitroso-β-naphthol, and also with the alkali metals by pseudo-indoxyl derivatives. The same grouping is found in indigo and in the γ-pyridones, and some of the peculiarities of these compounds may be due to the formation of chelate rings.

Class IV. This occurs in the dioximes of α-diketones, as in the well-known dimethyl-glyoxime compound used for the quantitative estimation of nickel. Tschugaeff, who discovered this reaction, originally assumed that the metal was attached to the oxygen of the second as well as to that of the first oxime group ; this would give a very improbable 7-ring. Later he showed that it was more likely to be joined to the nitrogen of the second oxime group, the structure being



and so forming a 6-ring. He confirmed this by showing that similar chelate compounds are formed by the oxime of α-acetyl pyridine

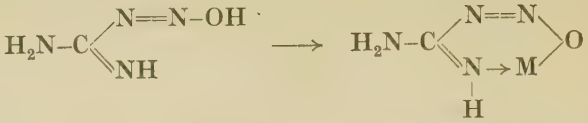


Class V. This is present in the compounds of mordants with azo-dyes having a hydroxyl in the ortho-position to the azo-group. Certain mordant dyes derived from hydroxy-pyrazolone also belong to this class. The same ring (except for a shift in the position of the double links) occurs in one of the stereoisomers of the hydrazone of glyoxylic ester and of camphor quinone.[1]

Class VI. This occurs in the metallic (nickel, copper, palladium)

[1] Taylor and Ewbank, *J. C. S.* 1926, 2821.

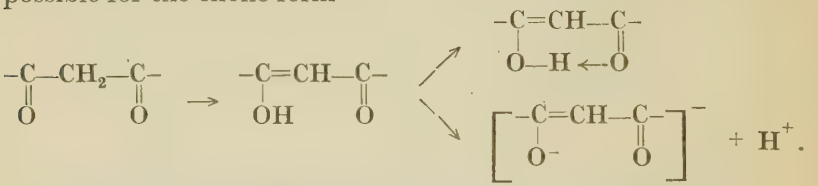
derivatives obtained [1] from nitrosoguanidine, presumably acting in the hydroxylic form :



Tschugaeff gives a slightly different formula, with an imine group outside the ring, and only one double link inside ; but for the stereochemical reasons given above, this seems less probable.

All these five classes contain the 6-ring with two double links (if we count the link in the aromatic nucleus as double) and no doubt owe their stability to the absence of strain in such a ring.[2]

Compounds of class I (free from nitrogen) are peculiar in that the organic substances which form chelate rings of this type most easily are also those which show a definite acidity [3] : roughly speaking the two properties seem to go together. It is clear that neither of them can be the direct result of the other, since chelation and ionization are two alternative reactions possible for the enolic form



[1] Thiele, *Ann.* 1893, **273**, 133 : Tschugaeff, *Ber.* 1906, **39**, 3388.

[2] Prof. T. S. Moore has, however, pointed out to me that although the 'natural angles' add up to 720°, as do those of a hexagon, the ring is not symmetrical owing to the positions of the double links, and if the angles are all to be strainless the sides cannot be equal : thus in class V above, if the other five sides are of equal length, the side M—O will be 1·49 times as long. If the six sides are all equal (i.e. if the six atoms of the ring all have the same diameter), the angles will all be 120°, and so the strain on each doubly linked atom will be + 5° 16′, as in Kekulé's formula for benzene, and that on each of the two which are not doubly linked will be, if the ring lies in a plane – 10° 32′. This suggests that chelate rings of this type should be especially stable when M is a large atom, and such compounds no doubt are stable, but so are those with small atoms such as beryllium. It will be noticed that this form of ring (apart from the co-ordinate link) also occurs in the ortho-quinones. In the para-quinones the double links are symmetrically disposed, and hence there is no strain if all the sides are equal. This may explain the greater stability of para-quinones.

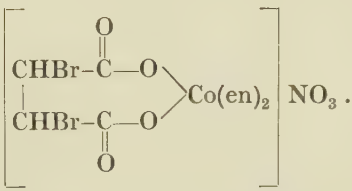
[3] The evidence for the acidity of these compounds needs, however, to be

Other things being equal, the occurrence of one of these reactions will diminish that of the other, as is shown by the fact that compounds containing the –C(OH)=CH–CO– group in such a position that chelation is impossible for steric reasons are unusually acidic.[1] The simultaneous occurrence of these reactions is no doubt due to two common causes. Firstly, any structure which tends to enolization will promote both. Secondly, the relative positions of the two oxygen atoms which are favourable to chelation are also those which promote ionization. As the ring in order to be stable with the two double links must contain six atoms, the second oxygen atom must be in the β-position with respect to the first. This gives us in the enolic form a grouping which differs from a carboxyl group only in the interposition of a –C=C– group :

On any form of the theory of alternating polarity it is to be expected that the acidifying influence of the carbonyl on the hydroxyl, which is so marked in the carboxylic acids, will be transmitted through this grouping.

7-RINGS AND 8-RINGS

Only a very few chelate rings of more than six atoms have been observed, and they all belong to type A. Duff has shown [2] that cobalt can form 6-covalent compounds in which two of the positions are occupied by the anion of a β-dicarboxylic acid such as succinic, dibromosuccinic, maleic, itaconic, &c. This involves the presence of a 7-ring, as in

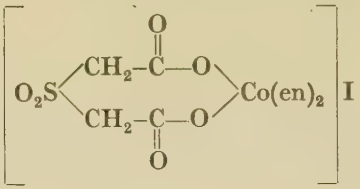


scrutinized with some care. The ordinary equations for ionic equilibria, for example, in the hydrolysis of salts, no longer hold when the base is capable of forming non-ionized complexes with the acid.

[1] For example, ethyl cyclobutenolone carboxylate (Taylor and Ewbank, *loc. cit.*) and dimethyl dihydro-resorcinol and the β-diketo-cyclopentane derivatives. (See Bennett, *Chem. and Ind.* 1926, 960.)

[2] *J. C. S.* 1921, 119, 385.

Previously Price and Brazier had found [1] that sulphonyldiacetic acid gave similar chelate compounds such as



which thus contains an 8-ring.

The molecular weights of these substances have not been determined, nor their ionization measured; but there seems little doubt that they are correctly formulated. Their occurrence is peculiarly interesting in view of the failure of all attempts to obtain such 7- or 8-rings of other types.

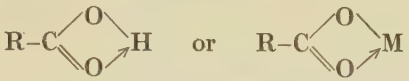
Co-ordination and the Carboxyl Group.

The question whether the carboxyl group can form chelate rings is one of some interest, and may be considered here. The precise structure of this group has been much discussed. In many ways the C=O in an acid does not behave like an ordinary carbonyl group.[2] It does not give the carbonyl reactions with phenyl hydrazine or hydroxylamine; it is much less easily reduced; its refractive power [3] and its parachor [4] are less than we should expect. Two adjacent carbonyls in the α-diketones give the compound an intense yellow colour, as we see in diacetyl, glyoxal, and benzil; but pyruvic and oxalic acids are colourless. These and similar reasons have led to the belief that the hydrogen in the carboxyl group is in some way attached to both oxygen atoms, which is commonly expressed by saying that it is co-ordinated with them. It is, however, to be observed that most of the above-mentioned peculiarities are shared by the esters, and these must have some other explanation, since co-ordination in this sense is not possible with the esters.

Whatever may be the explanation of these facts, it is obviously worth while to inquire into the evidence for co-ordination in the carboxylic acids and their metallic derivatives. On general grounds it might be expected to occur. The hydrogen of a hydroxyl group, when it is not too acidic, is well known to be able to act as an acceptor, and so is the metallic atom which

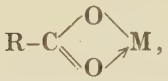
[1] *J. C. S.*, 1915, **107**, 1367. [2] See Smedley, *J. C. S.* 1909, **95**, 231.
[3] Brühl, *Ber.* 1907, **40**, 896. [4] See p. 126.

replaces it. The carbonyl group readily acts as a donor: in fact these two groups are the cause of the ring-closure in the compounds we have just been considering. The abnormal properties of the carbonyl group in the free acids lend further support to the idea of ring formation. Nevertheless there is strong evidence that rings of the type of

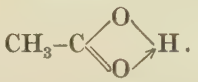


cannot exist, and that while the two groups —OH and —C=O are very ready to form a co-ordinate link as acceptor and donor respectively, they cannot do so within the limits of a single carboxyl group, because the strain in the resulting 4-ring would be too great: there is no example of a ring of this size and this type, consisting solely of elements with a covalency maximum less than six.

Consider first the behaviour of acetic acid. We have already seen that a group capable of forming a chelate ring with a metallic atom can almost always do so with hydrogen, so that if the acetates (and the salts of carboxylic acids in general) can form a ring



acetic acid should form a similar ring

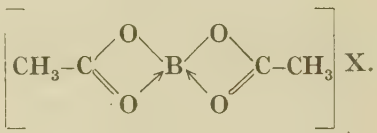


The properties which this compound would have we know already from the analogy of such substances as acetoacetic ester and ortho-nitrophenol. It would have a relatively low boiling-point, and the association which the hydroxyl group normally causes would be suppressed. The actual properties of acetic acid are the opposite of this. Its boiling-point is 40° higher than that of the alcohol with the same number of carbon atoms, and 60° higher than that of its methyl ester. The following table shows the effect of methylation of the hydroxyl on the boiling-points of these compounds:

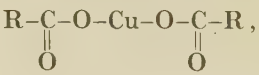
Boiling-point of	*R·OH*	*R·OCH$_3$*	*Diff.*
Ortho-nitrophenol	214°	265°	+51°
Para-nitrophenol	295°	259°	−36°
Acetic acid	118°	58°	−60°
Benzoic acid	249°	199°	−50°

Acetic acid can be shown to be associated, not only in the pure liquid and in non-associated solvents, but even in the vapour. Its behaviour is exactly parallel to that of para-nitrophenol: it is the behaviour of a substance containing in the molecule a donor and an acceptor, both active, but prevented by their position from reacting with one another, in the meta and para substituted phenols because they are too far apart, and in the carboxylic acids because they are too near: so that the co-ordinate link can only be formed between two molecules, and polymerization (association) results.

In the simple acetates again we find no evidence of co-ordination. They are not always salts: they are sometimes covalent (i. e. they behave like esters), but that is a very different matter. They follow the type of the halides rather than that of, say, the acetylacetonates. Thus boron forms $B(O{\cdot}CO{\cdot}CH_3)_3$, which does not behave as a salt, but rather like the trichloride; on the analogy of the acetylacetonate it should form a salt



Lowry and French have shown [1] that the cupric derivatives of the higher fatty acids behave as non-polar compounds, and are more soluble in non-hydroxylic solvents than in water. They conclude that these are chelate compounds, in which the copper forms part of two 4-rings. But their evidence does not prove anything more than that these copper derivatives can exist in a covalent form

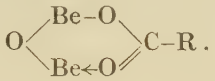


analogous to the boron compound.

The only acetates whose formulae indicate that the carboxyl group occupies two co-ordination positions have structures which allow of the two oxygen atoms of each carboxyl group attaching themselves to two different atoms, so as to form a ring of more than four members. One example is the ' basic ' beryllium acetate with its analogues. In these compounds the carbonyl oxygen does not join itself to the metallic atom attached to the

[1] *Proc. Roy. Soc.* **1924, 106,** 489.

other oxygen of the same carboxyl but to another one, and a 6-ring is formed through the central oxygen



A similar arrangement must occur in the complex iron and chromium derivatives of the carboxylic acids. It is remarkable that iron never forms simple salts of the type $Fe[O{\cdot}CO{\cdot}R]_3$ at all,[1] but invariably complex compounds, and that these always have more than one, and nearly always three, iron atoms in the molecule. Thus the blood-red solution obtained on testing for an acetate with ferric chloride contains the salt

$$[Fe_3(OH)_2(O{\cdot}CO{\cdot}CH_3)_6]O{\cdot}CO{\cdot}CH_3.$$

Analogous chromium compounds occur, and even mixed derivatives, in which one or two of the iron atoms are replaced by chromium. The structure of these compounds is obscure, but it is at least clear that the co-ordination of the C=O of the carboxyl group is only possible when there is a second metallic atom in the molecule, so that a ring of more than four atoms can be formed.

[1] Weinland, *Komplexverbindungen*, p. 349.

XV

THE PERIODIC GROUPS

WE have already considered the relation of the periodic classification to the atomic structure (Ch. III, pp. 38–47), and the bearing of this on the chemical characteristics of the periodic groups (Ch. V) and on the tendency of the elements to ionize (Ch. VI, p. 104). The detailed application to the individual elements and their compounds of the principles of valency at which we have arrived will be the subject of the next volume. It may, however, be useful at this point, even at the cost of some repetition and some anticipation, to give a brief account, in the light of what has already been said, of the more important valency relations of the several groups of the periodic table.

The form of periodic table most suitable for this purpose has already been given (Ch. V, p. 75) and its relation to the Bohr theory discussed. In this table, which is essentially that of Mendeléeff, the elements are divided into nine groups (O—VIII), all but the first and last of which consist of two typical elements and two subgroups A and B. Generally speaking, in the Nth group the members of the A subgroup contain N more electrons than the preceding inert gas, while those of the B subgroup have $8-N$ electrons less than the next following inert gas. Hence in the first two periods, in which each inert gas has 8 electrons more than its predecessor, the same element represents the A and B subgroup : these are the typical elements. An obvious modification of this scheme is required in the rare earth period, owing to the expansion of the antepenultimate fourth quantum group of electrons from 18 to 32. The conventional name of eighth group is retained for the three transitional triads, although this group should strictly be divided into three, the eighth group proper (iron, ruthenium, osmium), a ninth group (cobalt, rhodium, iridium), and a tenth group (nickel, palladium, platinum).

As it will often be necessary in this chapter to give numerical values of the ' valency ' of elements, the reader may be reminded that this term is used in the sense defined in the last section of Chapter X (p. 182), as equal to the diminution in the number of unshared electrons in the atom caused by its state of combination. This value is not affected by co-ordination or complex

formation when the atom in question acts as an acceptor, nor in the case of a cation by the conversion of a covalency into an electrovalency (ionization); in the oxy-compounds it is the same whether we regard the atom as joined to a single oxygen atom by a double link or by a co-ordinate link. Thus the valency of iron is three in

in

in $K_3[Fe(CN)_6]$, and in $[Fe]Cl_3$; and that of sulphur is 6 in

and in

GROUP O: INERT GASES

He 2 Ne 10 A 18 Kr 36 X 54 Em 86.

Only the first of these calls for any comment, or can be said to have any chemical properties. The spectrum of neutral helium consists of two apparently unrelated spectra, known as the parhelium and orthohelium spectra; the latter, since its intensity can be increased by appropriate electrical excitation, is evidently due to a second (excited and metastable) state of the neutral atom. Bohr showed that whereas the stable parhelium atom has both its electrons in 1_1 orbits, the ortho-form has the second electron in a 2_1 orbit, from which, by the correspondence principle (p. 34), it cannot return to the more stable 1_1 orbit directly, but only by collision. Hence it is possible by suitable electrical treatment to convert a considerable proportion of the helium into this form. Orthohelium, having one electron much more loosely held than the other, should be a univalent element resembling hydrogen in its properties, and hence with analogies to the alkali metals; its spectrum is similar to that of lithium. Various attempts have been made to induce excited helium to enter into chemical combination, and it has been proved to form a fairly stable solid compound with tungsten (apparently WHe_2), and probably at low temperatures very unstable solid compounds with iodine, sulphur, and phosphorus. It also forms a gaseous compound with mercury of uncertain composition (we should expect $HgHe_2$), and there is some reason to think that it can polymerize to He_2.

GROUP I

Hydrogen

Hydrogen may be included either in group I or group VII : in either case it is so peculiar as to need special treatment. It occurs in combination in five forms : (1) as a cation $[H]^+$; (2) as an anion $[H]^-$; (3) as a uni-covalent atom H—, attached by two shared electrons ; (4) rarely in a covalent form attached by a single shared electron ; (5) as a co-ordinated divalent atom —H←.

(1) The simple hydrogen ion, consisting of a single proton, is probably rare, most acids being covalent in the pure state, and the ion in dissociating solvents being almost invariably solvated, and therefore in condition (3) or (5).

(2) The negative hydrogen ion occurs (p. 64) in the hydrides of the alkali and alkaline earth metals.

(3) The marked tendency of hydrogen to pass from the ionized to the covalent state, to which the weakness of weak acids is due, is to be expected on the Fajans theory, since hydrogen is the extreme case of a small cation. It may also be explained, as Lewis suggests, as being due to the fact that hydrogen alone among cations is satisfied with the pair of shared electrons which it obtains by forming a covalency with its anion.

(4) The peculiarities which on physical grounds we should expect hydrogen to show, owing to its core consisting of a single proton with no attached electrons, are comparatively little apparent in its chemical behaviour ; but there is reason to think (p. 102) that it is the one element which can be covalently linked by means of a single shared electron ; this form of link is only known to occur between hydrogen and hydrogen (as in H_2^+) or between hydrogen and boron, and is always very unstable.

(5) The evidence for the existence of co-ordinated 2-covalent hydrogen has been discussed (p. 72) ; it can only act in this way as an acceptor when it is already united to a suitable atom, usually either oxygen or fluorine.

Group I : Elements other than Hydrogen

These elements, with their atomic numbers and atomic volumes (in the elementary state) are as follows :

Li 3	Na 11	K 19	Rb 37	Cs 55	(87)	A
11·8	23·7	45·3	56·0	70·7	—	
		Cu 29	Ag 47	Au 79		B
		7·1	10·3	10·2		

Characteristic structures : A : (C) (8) 1
B : (C) (18) 1

In these structures the symbol (C) stands for an inner core of completed electronic groups ; in lithium of course the structure is (2) 1.

The typical elements are very closely related to the A subgroup; the resemblance of the B subgroup amounts to little more than the power of forming univalent cations (copper and gold very unwillingly). The enormous difference in atomic volume between the alkali metals and the elements of subgroup B is of great importance. The much greater size of the former is a sign that their valency electrons are in a much weaker field than those of the latter, or in other words, that the group of 8 electrons is much more efficient (in proportion to its number) in screening the outer electrons from the field of the nucleus than the group of 18. In the ions, where the valency electrons are removed, the difference is much less [1] but it is in the same direction. This difference in the external field, and hence in the size, is the cause of the greater tendency of the B elements of all the earlier periodic groups to form covalent compounds.

Group I : Typical Elements and Subgroup A : Alkali Metals

The properties of these elements are mainly governed by a strong tendency to ionization, since by the loss of single electron the atom can assume the stable structure of an inert gas. Such salts as the halides are always ionized, even in the solid state. The covalent condition is more readily assumed by the ion than by the neutral atom, and almost the only stable examples of it are found among the hydrated salts. These illustrate a tendency characteristic of every group of metals, that the lightest members, although the maximum number of water molecules that they can take up is smaller than with the heavier (according to the covalency rule), reach this maximum with greater ease. This agrees with Fajans' theory, of which the alkali metals, with their large size and their single charge, are striking examples : the formation of covalent links is excessively difficult for all but the smallest members. Accordingly we find that the salts of lithium are nearly all hydrated, and most of those of sodium, while

[1] The 'volume' of an ion is not a fixed quantity, but varies with the nature of the other ion present, and in crystals with the nature of the lattice, so that it is of little use to give numerical values.

those of potassium are usually, and those of rubidium and especially caesium almost invariably anhydrous. Covalent compounds of neutral atoms of this series are rare; they are found in the uni-covalent alkaline alkyls and aryls of Schlenk (p. 154) such as sodium methyl $Na–CH_3$ and sodium phenyl $Na–C_6H_5$ (sodium benzyl however is a salt $Na[CH_2{\cdot}C_6H_5]$), which are very unstable, being spontaneously inflammable in air. The covalent alkaline atom is more stable when it attains by co-ordination a covalency of four or six: this occurs in the chelate compounds of β-diketones and similar substances (p. 145), among which compounds of 4-covalent lithium, sodium and potassium, and of 6-covalent sodium and potassium are known.

Subgroup I B: Copper, Silver, Gold

These elements resemble the alkali metals in having one electron more easily removed than the rest, but differ from them in that the next electronic group contains 18 electrons instead of 8. Thus they are all capable of a valency of one: but the 18 group is less stable than the 8, and it is possible under some conditions to utilize some of its electrons for valency purposes, so that we find the higher valencies of 2 in copper and 3 in gold. We may consider first the univalent compounds, in which alone these elements are comparable with the alkali metals. The small size of their ions makes them (and especially copper, the smallest of them) much more ready than the alkali metals to form covalent links. Although the halides are ionized in water so far as they dissolve, and in the fused state (cuprous chloride only partially), the cuprous have non-ionic lattices in the crystals, and so does silver iodide at the ordinary temperature, and cuprous chloride is bimolecular (and therefore covalent) in the vapour. In the same way these elements all have a marked tendency to form complex ions, as in $K_2[CuCl_3]$, $[Ag(NH_3)_2]Cl$, and $K[Au(CN)_2]$. The value of the covalency in these complexes seldom exceeds 3 and never, so far as is known, 4.

The existence of cuprous salts is limited by the possibility of the reaction

$$2\,Cu^{+} \;=\; Cu^{++} + Cu,$$

the equilibrium between the two ions being much in favour of the cupric (the cuprous ion has been shown to be Cu^{+} and not Cu_2^{++}). Thus a cuprous salt readily soluble in water without forming complexes, and so giving a high concentration of cuprous

ions, would decompose into the cupric salt and metallic copper : this happens with cuprous sulphate, which can be made in the absence of water (from cuprous oxide and dimethyl sulphate), but is at once decomposed by water with separation of copper. Similarly cuprous nitrate, which cannot be obtained as such, can exist in the complex $[Cu(CH_3{\cdot}CN)_4]NO_3$. The stable cuprous compounds, such as the halides, are those which are practically insoluble in water, and only dissolve in presence of something (such as hydrochloric acid, soluble chlorides, or ammonia) with which they can form complexes. In the same way the aurous ion can only exist in very small concentration, and the salts readily pass into auric compounds and metallic gold. The stability of the silver ion, which is unique among the univalent ions of this subgroup, is no doubt due to the fact that the silver atom cannot lose (or share) more than one electron, or, as we should ordinarily say, that there is no higher state of oxidation into which it can pass.

The occurrence of higher valencies among these elements is due to the weakness of the electronic group of 18 as the outer group in a univalent ion. In copper, one of the electrons of this group can be ionized or shared, in silver none, and in gold two can be shared but not ionized without great difficulty : there is no satisfactory proof of the existence of the auric ion Au^{+++}. Why there is this difference between the three elements we do not know. The spectroscopic evidence shows that the stability in the neutral atom of a penultimate group of more than eight electrons is greater when it is in the fourth quantum group (in the series Nb—Ag) than when it is in the third (Ti—Cu) or the fifth (Ta—Au).[1] This is not an explanation of the difference between copper, silver and gold, but it shows that it is part of a more general phenomenon. The explanation will no doubt come when the dynamics of the atom are more fully understood. With the breaking down of the 18 group the properties associated with imperfect groups in the core appear, the colour and the paramagnetism.

The cupric compounds should be compared not with those of the alkali metals, but with those of the divalent transition elements such as nickel, or, apart from their transitional properties, with those of zinc. Like the latter, they are distinguished from the alkaline earth compounds by their much stronger tendency to form covalent compounds and complex ions. This

[1] See list of atomic structures, p. 49.

is explained by the small size and double charge of the ion. Among the neutral compounds are those of the β-diketones and β-ketoesters, which have recently (see p. 226) been shown to be optically active; of the numerous complex ions the best known are those of the cuprammonium salts $[Cu(NH_3)_4]X_2$. It is remarkable (and unexplained) that compounds with a covalency of more than four, although they are known, are comparatively rare, much rarer than with magnesium or calcium.

The auric compounds are all covalent; auric chloride is practically not ionized, though it dissolves in hydrochloric acid to give the very stable auric acid $H[AuCl_4]$. Here also, as with the cupric compounds, although covalencies of 5 and 6 are known, they are much less common than those of 3 and 4.

GROUP II

Elements and Atomic Volumes

		Ca 20	Sr 38	Ba 56	Ra 88	A : (C) (8) 2
Be 4	Mg 12	25·4	35·1	36·7	–	
4·92	14·0					
		Zn 30	Cd 48	Hg 80		B : (C) (18) 2.
		9·5	13·0	14·1		

The contrast between the subgroups is less marked than in group I. In the A subgroup the core is still unalterable, and of the number of an inert gas; the expansion of the penultimate group which occurs in the transition elements has not yet begun. In the B subgroup the nuclear charge (which is now two units more than corresponds to the core, whereas in I B it was only one more) holds the 18 group so firmly that it is never broken into either by ionization or sharing. Thus both subgroups have unalterable cores and constant valency.

We still, however, have the outermost electrons in the atoms of the B subgroup moving in a stronger field than in those of the A, with a consequent diminution of atomic volume. Accordingly the tendency is much stronger to ionization in A, and to complex formation in B. This is illustrated by the electrode potentials :—

Be	Mg	Ca	Sr	Ba
?	−2·54 ?	−2·56	−2·77	−2·8
	Zn	Cd	Hg	
	−0·49	−0·40	+0·75	

The ionization tendency in the alkaline earth metals calcium,

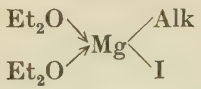
strontium and barium (and radium, so far as we know) is so strong that it determines most of their behaviour, as it does with the alkali metals. Of the typical elements, beryllium, as we should expect from its abnormally small volume, resembles the B rather than the A subgroup ; magnesium has affinities with both.

There are indications that the normal covalency is in the A subgroup 6 rather than 4, and in the B subgroup 4 rather than 6.

Group II : Typical Elements and Subgroup A : Beryllium, Magnesium, and the Alkaline Earth Metals

Beryllium, owing to the small size of its atom, is very different from the other elements. It is on the limit of ionization. Its chloride, though ionized in water, is a poor conductor in the fused state ; its oxide, unlike those of magnesium and calcium, has a non-ionized lattice. The beryllium ion has a strong tendency to combine with four molecules of water or ammonia ; it forms complexes with the greatest readiness, the oxalate being apparently an auto-complex $Be[Be(C_2O_4)_2]$, while the normal acetate $Be[O{\cdot}CO{\cdot}CH_3]_2$ is unstable and easily changes into the ' basic ' acetate $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$, a purely covalent compound.

Magnesium has much more resemblance to the alkaline earth metals than beryllium. It has some tendency to complex formation, as is shown by the cationic mobility ratio of magnesium sulphate, which changes from 0·40 in 0·05 molar to 0·26 in 1-molar solution. It usually occurs as the ion, which readily takes up 6 molecules of water. On the other hand it assumes the covalent form in the Grignard reagent, which has been shown to contain normally in the solid state two molecules of ether, so that it no doubt has the structure



The remaining elements, calcium, strontium, barium and radium, form a very well-marked series, with a much smaller tendency to form complexes, which is perceptible in the lighter members, but falls off as the atomic number increases, as does also the tendency to hydration.

Subgroup II B : Zinc, Cadmium, Mercury

These elements are uniformly divalent (the mercurous ion is only an apparent exception), having an unalterable core two less than the atomic number both in the ionized and in the covalent

compounds. The small size of the ions, together with their double charge, makes them very ready to pass into the covalent state. The halides, for example, have much less of the character of salts than those of the alkaline earths ; they are more volatile and more soluble in organic solvents, and their conductivities in the fused state are low, those of the mercuric halides very low. The same preference for the covalent state is shown in water ; zinc salts form complexes readily, cadmium salts with unparalleled ease, and mercuric salts, although they do not form auto-complexes, are largely present in the un-ionized state.

Mercury occupies a unique position among the metals. It readily forms covalent links of great stability with a variety of elements, especially the halogens, oxygen, nitrogen, and carbon ; far more ' organic ' compounds are known of mercury than of all the other metals together. Its stability in the covalent state is shown most conclusively in the mercurous ion, which has been proved by a variety of methods to be diatomic, consisting of two atoms which have each lost one and shared the other electron. The mercurous compounds seem to be confined to those in which the metal is attached to a halogen or to oxygen (oxide and salts of strong oxy-acids), and in this state the metal never seems to have a covalency of more than two. The mercuric compounds show a further peculiarity. Not only do they ionize to a very minute extent (except those of the strong oxy-acids), but unlike the cadmium compounds they have very little tendency to form auto-complexes : mercury is for some reason far more stable with a covalency of two, and far less ready to increase it to four, than any other metal. This may explain the fact that mercuric salts are almost invariably anhydrous.

GROUP III

Elements and Atomic Volumes

		Sc 21	Y 39	La 57	Ce 58	Pr 59	Lu 71	Ac 89
B 5	Al 13	11·6	—	22·5	20·0	21·8		
4·11	10·2	Ga 31	In 49				Tl 81	
		14·9	15·5				17·3.	

Characteristic groupings :

A : (C)(8 + 1) 2. B : (C)(18) 2, 1.

The contrast between the subgroups is still less in this group, and the typical elements resemble the B subgroup more ; the

18 group of electrons in subgroup B attains a greater stability as the number of valency electrons (and so the excess of the nuclear charge) increases. This can be seen from the much smaller differences in atomic volume.

We find for the first time in this group (and in every member of it) that the valency electrons do not all occupy the same type of orbit. In the typical and B elements there are two N_1 orbits and one N_2 : in the elements of the A subgroup two are in the electronic group of highest quantum number, and one is in the next group (for example, in scandium, $2 \times 4_1$ and $1 \times 3_3$), and this arrangement of the two outermost electronic groups persists throughout the whole of the rare earth metals. Of this difference in the orbits of the valency electrons there is little trace in the chemical behaviour of the typical and A elements, but in the B subgroup there are signs of the two N_{11} electrons refusing to act as valency electrons (the ' inert pair '), in univalent indium and thallium.

The typical elements resemble the A subgroup in having the three valency electrons ' backed ' by an electronic group of 8, and the B subgroup in having all three in the same quantum group ; they thus have resemblances to both subgroups, but do not quite belong to either. They also have peculiarities of their own, since with the increased valency the tendency to covalency formation predominates exclusively in boron, and considerably in aluminium. The B subgroup differs from the A in being less electropositive, as we should expect from the somewhat smaller atomic volume ; the metals also have lower melting-points, and the halides are more volatile.

Typical Elements : Boron, Aluminium

Boron is the only element with less than four valency electrons which cannot form a simple cation (owing to its small size) ; it is also the only element more than four places before an inert gas which gives volatile hydrides, these being of a peculiar type,[1] such as B_2H_6, in which the boron is apparently quadrivalent : they can only be explained by supposing that some of the hydrogen atoms are attached by 1-electron links. Otherwise boron behaves as a normal trivalent element, which readily completes its octet by co-ordination. Its halides, including the fluoride, are volatile and non-associated (for a possible reason

[1] See p. 103.

see p. 245); they are non-conductors. They are hydrolyzed by water to the very stable boric acid $B(OH)_3$, which is remarkable for its extreme weakness (its first dissociation constant is $1{\cdot}7 \times 10^{-9}$, about the same as that of hydrocyanic acid, and only about one-fifth of that of hydrogen sulphide), and for the great rapidity (only equalled by that of nitrous acid) with which its esters and acyl derivatives are formed and hydrolyzed. Of the numerous co-ordinated and chelate compounds of boron, many have already been mentioned (pp. 155, 222).

Aluminium, having a larger atom than boron, can form a trivalent cation Al^{+++}, but it readily assumes the covalent state, and as readily increases its covalency from 3 to 4, and less readily to 6, by co-ordination. The ion, owing to its triple charge, easily takes up 6 molecules of water, and also quite frequently 12, presumably in the form of double molecules (p. 199). The hydroxide $Al(OH)_3$ is amphoteric in character, forming aluminates; it is in fact almost as much an acid as boric acid, and the so-called aluminium alkylates, which are volatile (e.g. $Al(OC_2H_5)_3$, M.Pt. 130°, B.Pt. 205° under 14 mm.) are esters like the boric esters. The halides, except the fluoride, though they ionize in water, are clearly themselves covalent compounds, being very bad conductors; their boiling-points are raised by their polymerization, which is shown in the vapour and in non-dissociating solvents. They form addition compounds with great ease with almost every class of organic compound, usually of the 1 : 1 type, as in $R_2C{=}O{\rightarrow}AlCl_3$. The reactivity which the organic component often exhibits in these compounds is the basis of the Friedel-Crafts reaction.

Subgroup III A: Scandium, Yttrium, and the Rare Earth Metals

All these are transition elements in the wider sense of the term, since the neutral 'normal' atom contains an imperfect inner group (2, 2, 4, 1); as such they are included in the frames in Bohr's table (p. 39). But chemically they have little of the properties of transition elements. The last electron in the penultimate group is almost as loosely held as the two in the outermost group, and acts entirely as a valency electron. They therefore behave, so far as the two outer electronic groups are concerned, as trivalent elements with a complete core—in the scandium ion Sc^{+++} (2)(8)(8) and in the lanthanum ion La^{+++} (2) (8) (18) (18) (8); thus they are colourless and diamagnetic,

with the exception of the elements from cerium (58) to ytterbium (70), which are transitional for a different reason, owing to the imperfection of the antepenultimate (fourth quantum) group. These last all have the structure (2) (8) (18) (18+X) (2, 2, 4, 1), in which X varies from 1 in cerium to 13 in ytterbium. This imperfect group gives them their peculiar optical and paramagnetic properties (pp. 43, 214), but it is too far within the atom to affect the chemical properties seriously, except in the first two elements, cerium and praseodymium. All the rest have the group valency of 3 ; but cerium forms a definite series of quadrivalent ceric compounds, such as an oxide CeO_2 and a nitrate $[Ce](NO_3)_4$, which are easily reduced to the cerous state, but are fairly stable. Corresponding quadrivalent praseodymium compounds are known, but they are much less stable, and immediately oxidize cerous compounds to ceric. The later members of the series show no sign of becoming quadrivalent. This is because a new type of orbit is always less stable in the first elements in which it appears than in the later ones. When (in Ce 58) the nuclear charge is just large enough to draw an electron into a 4_4 orbit, this is not much more difficult to remove than the three valency electrons in 5_3 and 6_1 orbits ; but as the nuclear charge increases, the removal becomes less easy : it is just possible with praseodymium (59), but not with the succeeding elements.

Of the properties of this subgroup in general, apart from the peculiarities of the rare earth metals, there is not much to be said. The elements are more electropositive than those of subgroup B, as would be expected from their larger atomic volumes ; the hydroxides are less acidic, and do not dissolve in alkalis like those of the B elements ; the halides are less volatile, and the metals form stable carbonates, which those of subgroup B do not.

Subgroup III B : Gallium, Indium, Thallium

The elements of this subgroup, in addition to being less electropositive than those of A, are remarkable for showing valencies lower than three. Gallium can be divalent, indium di- and univalent, and thallium univalent : that is, one of the three valency electrons in gallium, one and two in indium, and two in thallium can become inactive. The inactivity of two electrons may fairly be taken to be an example of the independence of the N_{11} group of outer electrons, for which the Stoner theory gives a reason (see p. 35) : there are many examples of

this in the later periodic groups. The presence of a single inactive electron in divalent gallium and indium is difficult to explain. The compounds in which these lower valencies are exhibited, except those of univalent thallium, are all very unstable, and they are almost confined to the halides. Gallous chloride $GaCl_2$ decomposes water with liberation of hydrogen, while indium dichloride $InCl_2$ and monochloride InCl are converted in water (like cuprous salts) into the trichloride and metallic indium. All these three chlorides give a vapour of the normal density; they are fairly good conductors in the fused state, which indicates the existence of the corresponding ions Ga^{++}, In^{++}, and In^{+}.

The thallous compounds (no compounds of divalent thallium are known) are much more stable, and show little tendency to go over into the thallic state. The ion has been shown to be partly but not wholly polymerized in solution to $[Tl_2]^{++}$ (presumably $^{+}Tl{=}Tl^{+}$), and almost the only known thallous compounds apart from the salts appear to be the curious liquid alkylates Tl–O–Alk and the acetylacetonate TlA : no complex compounds of univalent thallium are described. In all these respects the thallous compounds resemble the mercurous.

It is remarkable that thallium forms no mono- and no trialkyl derivatives, but only the salts of dialkyl thallium, such as $[(CH_3)_2Tl]I$, a very stable compound derived from a strong base $[(CH_3)_2Tl]OH$.

GROUP IV

Elements and atomic volumes :

		Ti 22	Zr 40	(Ce 58, Pr 59)		Hf 72	Th 90
C 6	Si 14	13·7	21·8	20·0	21·8	(ca.23)	20·8
7·6	11·4						
7·3		Ge 32	Sn 50			Pb 82	
		13·2	16·5			18·2.	

Characteristic groupings :

A : (C) (8, 2) 2. B : (C) (18) 2, 2.

The tendency for ions with a charge as great as four units to pass into the covalent state can only be overcome when they are unusually large, and hence we do not find quadrivalent ions of any stability among the elements of this group until we reach the second long period (tin, and perhaps zirconium); the quadrivalent compounds of the earlier elements are all covalent.

The main peculiarity of this group is due to the fact that since

there are four valency electrons, the atoms can, by the direct production of four normal covalencies, acquire the exceptional stability given by the fully shared octet ; they therefore tend to rest content with this state, and not to increase their covalency by co-ordination ; this is especially true of the lighter elements, and the B subgroup generally. In the first member, carbon, this group covalency is at the same time the maximum covalency, and as a result compounds of quadrivalent carbon are peculiarly stable, since the atom has the stability of the fully shared octet, and further is unable to act either as donor or as acceptor. This is one main reason for the unique position of carbon.

The characteristic difference between the subgroups which was observed in the previous groups—that A was more electropositive than B, and had less tendency to form covalencies—grows weaker in each successive group, and in the fourth has practically disappeared, as has also the difference in atomic volume. Indeed the atomic volumes of the B elements are now somewhat the larger, owing probably to the difference in crystal structure : carbon, silicon, germanium and tin crystallize in the diamond form, while all the A elements have a close-packed structure.[1] The two subgroups are sufficiently unlike in certain points, but it is a new kind of unlikeness ; it is mainly due to the transitional character of the A elements (which is further discussed below) and to the greater preference of the B elements for the 4-covalent state. This preference, which is not understood, is shown in the difference of crystal structure mentioned above, and still more clearly in the much smaller volatility of the halides of the A elements, with the exception of titanium. The most striking difference is that the typical and all the B elements form volatile hydrides and volatile alkyl derivatives, while none of the A elements do so ; this difference is found in all the subsequent groups. In all the points which distinguish the subgroups, the typical elements resemble the B subgroup and not the A.

The most important of these distinctions depend on the changes of valency. Practically all the elements of the group are capable of a lower valency than four, but this is due to different causes, and exhibited in a different way, in the two subgroups. In the A subgroup we find the characteristic behaviour of transition elements, due to the possibility of some of the outer electrons (two in this group) acting either as valency electrons or as a part of the core : this leads to the lower valencies of three and two.

[1] See p. 107.

In the B subgroup (and in the typical elements) no such electronic rearrangement is possible, and we might have anticipated that the valency would be invariably four ; but the two valency electrons of the N_{11} grouplet show in these elements a peculiarly strong tendency to become ' inert ' and act as part of the core. These two effects can lead ultimately to the divalency of the elements of both subgroups, but the results differ in two ways. The transitional A elements are more stable in the trivalent state than in the divalent, whereas in the B elements the trivalent state does not occur at all except as a ' forced valency ' in very unstable compounds such as the triaryl-methyls. Further, in the A subgroup the stability of the lower valencies diminishes as the atomic number increases (as happens in every group), whereas in the typical and B elements the opposite change occurs ; the inertness of the N_{11} pair is always more marked in the later members of a subgroup.

It will be convenient to consider first the typical and B elements and then the A subgroup. The following table, giving the boiling-points and conductivities of the tetrachlorides, and the action of water upon them, may be useful.

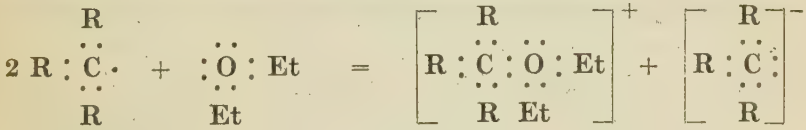
Tetrachloride of	*Boiling-point.*	*Conductivity.*	*Result of Action of Water.*
Carbon	76°	0	No action
Silicon	57°	0	Complete hydrolysis
Germanium	86°	0	Incomplete (reversible) hydrolysis
Tin	114°	0	Ionization (with some hydrolysis)
Lead	(ca. 150°)	8×10^{-7} (0°)	$Pb^{++} + 2\,Cl^- + Cl_2$ (and PbO_2).
Titanium	136°	0	$TiCl_3OH$, $TiCl_2(OH)_2$ $TiCl(OH)_3$, $Ti(OH)_4$
Zirconium	red heat	—	$ZrOCl_2$
(Cerium : non-existent)			
Hafnium	red heat	—	$HfOCl_2$
Thorium	ca. 1,000°	0·61(814°)	Ionization

Group IV : Typical Elements and Subgroup B : Carbon, Silicon, Germanium, Tin, Lead

Carbon is unique among the elements in the enormous variety of relatively stable compounds which it can form. Although silicon resembles it to some extent, we can now see that the organic chemistry of silicon, even if it were as fully worked out as that of carbon, would be found to be far less extensive. There are two main reasons for the exceptional position of carbon. The first is that in the 4-covalent compounds which it can form without co-ordination it not only has the great stability conferred

by the fully shared octet, but also is covalently saturated : the octet cannot expand. The atom is therefore unable to co-ordinate either as donor or as acceptor, and so is much less open to chemical attack, as we saw in comparing the action of water on the tetrachlorides of carbon and silicon (p. 157), or on chains of carbon and of silicon atoms (p. 159). This is the chief cause of the peculiar ' sluggishness ' (Trägheit) of carbon, a disinclination to react which gives comparative stability to a large number of thermodynamically unstable compounds. The second reason is that the affinities of carbon for a variety of other elements are much more evenly balanced than is usually the case : carbon has no very strong preferences, and hence can form compounds of the most diverse types which yet are reasonably stable. The link between one carbon atom and another is remarkably strong, and is little weakened by repetition, so that the element can form stable chains of enormous length. Further, it has almost as great an affinity for hydrogen as for oxygen. It is a general rule that the first member of a group has the strongest affinity for hydrogen and usually the weakest for oxygen (compare nitrogen and phosphorus, or fluorine and chlorine), and in carbon (alone of the fourth group elements) the two are so near that its link with hydrogen is not usually broken by such weak oxidizing agents as atmospheric air.

An important result of this exceptional stability of the normal 4-covalent state of carbon is that (except in the divalent derivatives, which are discussed later) it shows the greatest reluctance to abandon it. Trivalency, as in the triaryl-methyls, where the atom has a valency group of 7, only arises under extreme compulsion, and is excessively unstable. Ionization and co-ordination are unknown with carbon except as a means of escape from this trivalent state. If a trivalent derivative such as triphenyl-methyl is dissolved in a donor solvent like sulphur dioxide or ether, the latter forms a co-ordinate link with one trivalent atom, thereby increasing its valency group from 7 to 9 : one of these nine electrons is taken up by a second trivalent carbon atom, and two ions are formed, in each of which the carbon has regained a complete octet :



or more simply

$$2\ R_3C\ +\ OEt_2\ =\ [R_3C{\leftarrow}OEt]^+\ +\ [R_3C]^-.$$

The process is exactly similar to the conversion of an ammonia molecule into an ammonium ion and a free electron by addition of an atom of hydrogen : except that the nitrogen starts with a complete octet and the hydrogen adds one electron, while the carbon starts with a septet, and gains two electrons from the co-ordinate link ; in both cases since the valency group of 9 which would be formed is unstable, one electron is lost.

Among the general changes which occur in the series of elements from carbon to lead, the most obvious is the fall in the affinity for hydrogen, from the very stable hydrocarbons to the hydride of tin, which decomposes on standing, and that of lead, which is apparently even more unstable. Even with silicon the difference is considerable : its most stable hydride SiH_4 decomposes rapidly at 300–400°, and all the hydrides of silicon are decomposed by air, most of them being spontaneously inflammable. Silicon has a weaker affinity than carbon for hydrogen, for carbon, for itself,[1] and for nitrogen, but a stronger affinity for the halogens, and a much stronger for oxygen.

In their quadrivalent compounds the elements show the normal increase of metallic character with atomic number. This is indicated in the effect of water on the tetrahalides, and may be said to culminate in tin, where we get the stable stannic ion. The position of lead is different : its metallic character is indeed well marked, but it is manifested only in the lower valency : the compounds of quadrivalent lead are all covalent.

Every member of the series is known to form divalent compounds except silicon. It must however be remembered that though the compounds of divalent carbon are well known (as in carbon monoxide, the isocyanides and the fulminic derivatives, and the new diethoxymethylene $C(OC_2H_5)_2$), they are very few in comparison with the quadrivalent compounds, and it is quite possible that if the same amount of attention had been given to silicon it also would have been found to be capable of becoming divalent. At any rate, apart from carbon the stability of the divalent form increases with the atomic number. Divalent compounds are unknown with silicon, very unstable with germanium, fairly stable (though less so than the quadrivalent) with tin, and the only electrovalent form with lead. This increase in the inertness of the N_{11} pair is found in the later

[1] For a discussion of the mechanism by which the link of silicon to silicon is broken see p. 159.

periodic groups also. For some reason not yet understood, the inertness is peculiarly strongly marked in one vertical and in one horizontal series in the periodic table : in the series we are now considering, the typical and B elements of the fourth group, and in the successive elements following gold : mercury, thallium, lead, and bismuth (see p. 179). In lead, which is common to both of these series, it takes the peculiar form that the N_{11} grouplet (or at any rate two of the four valency electrons) is available for sharing but not for ionization : the only ions of lead are the plumbous Pb^{++}, while in the covalent compounds all four electrons are active. This is the cause of the remarkable reaction of lead chloride with zinc alkyls, in which metallic lead separates :

$$2\,PbCl_2 + 2\,Zn(CH_3)_2 = 2\,ZnCl_2 + Pb(CH_3)_4 + Pb.$$

It is of course on this change of valency that the action of the lead accumulator depends.

Subgroup IV A : Titanium, Zirconium (Cerium, Praseodymium), Hafnium, Thorium

This is the first group in which the A elements show the true transitional characteristics, with a variation of the valency by single units through the inclusion of one or more (in this group one or two) valency electrons in the core.

In the compounds with the group valency of four, there is the normal increase with atomic number of the metallic character, that is, of the tendency to ionization, culminating in thorium, whose tetrachloride shows no signs of covalency. In zirconium and hafnium, where the atom is presumably not large enough for ionization with a quadruple charge, a compromise is effected through the formation of the divalent ' yl ' ion $[X{=}O]^{++}$ (Zr=O, Hf=O), in which the metal, having only a double charge, can resist the tendency to form further covalencies. This kind of complex ion is not uncommonly formed by the A elements of the later groups. We do not know why the tetrahalides of zirconium and hafnium are so much less volatile than those of the B elements, nor why this difference does not extend to titanium. It is however clear that for some reason the A elements are less stable in the 4-covalent state than the B, and it is possible that this causes the halides to polymerize.

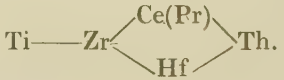
Cerium and praseodymium must be regarded as belonging to this subgroup in their quadrivalent state, though in the trivalent they belong to III A. When we examine the elements of sub-

group IV A in detail, it becomes obvious, both from the chemical point of view and from that of atomic structure, that they cannot be treated as a linear series Ti–Zr–Ce (Pr)–Hf–Th. The normal relation between the successive elements of a subgroup is that each has a whole quantum group in its core more than the one before it, and thus has its valency electrons in the next higher quantum group. This is the relation between titanium and zirconium, and between hafnium and thorium. But cerium and hafnium both have their valency electrons in the fifth and sixth quantum groups, and differ only in that the fourth (antepenultimate) quantum group contains 18 electrons in cerium and 32 in hafnium (with a corresponding increase of 14 units in the nuclear charge) :

22 Ti : (2)(8)(10)2
40 Zr : (2)(8)(18)(10)2
58 Ce : (2)(8)(18)(18)(10)2
72 Hf : (2)(8)(18)(32)(10)2
90 Th : (2)(8)(18)(32)(18)(10)2

(Cerium is here given not in the true ' normal ' form, but in the less stable form from which its quadrivalent compounds may be supposed to be derived.)

It thus appears that cerium and hafnium should be regarded not as successive links in a linear series, but as two alternative links between zirconium and thorium, the chain of elements being branched at this point :



Accordingly we find that the properties of quadrivalent cerium are not intermediate between those of zirconium and hafnium, but are in every way nearer to those of thorium. The properties of zirconium and hafnium are almost identical. The tetrahydroxides of zirconium and hafnium are weakly acidic, while those of cerium and thorium are not : the peculiar metastability of the forms of thorium sulphate is repeated with the ceric salt, but not with that of hafnium : the tendency to form double nitrates is common to thorium and cerium, but is not shared by hafnium. It is probable that the unparalleled resemblance between zirconium and hafnium, which is greater than that between any other two elements outside the rare earth series, and probably as great as that between any two of the rare earth

metals themselves, is at least partly due to this peculiar relation in structure, and that the increase of the fourth quantum group from 18 to 32, together with the increase in the nuclear charge, in some way neutralizes the effect of increasing by one the principal quantum number of the valency electrons. The resemblance recurs, though to a diminishing extent, in the pairs niobium and tantalum, and molybdenum and tungsten, which have similar structural relations.

The greater stability of the highest covalencies in subgroup IV A as compared with IV B is shown by the extreme rarity of a covalency of 8 in the B subgroup. In A, as soon as a covalency of 8 becomes possible, a whole series of 8-covalent compounds with β-diketones, &c., of the type MA_4 are formed ; they have been prepared with zirconium, cerium, hafnium, and thorium (see pp. 156, 169). No compounds of this type are known in subgroup B. Tin, which has been examined in great detail, forms some compounds in which it is 8-covalent, but they are all of more complicated types, and the same is true of lead. The difference in atomic volume (Zr 21·8, Ce 20·0, Th 20·8 : Sn 16·5, Pb 18·2), although it is in the right direction, does not seem large enough to account for this.

In the compounds in which these elements show a valency less than four, we find a tendency common to all transition elements, that in each group the stability of the lower valencies diminishes as the atomic number increases. Titanium is definitely trivalent (although the compounds readily pass into the quadrivalent state), and must be divalent in the dichloride and diiodide, although their molecular weights are unknown. Zirconium was until lately supposed always to be quadrivalent : trivalent and even divalent zirconium compounds have recently been prepared (as a trichloride and a dichloride), but they are less stable than those of titanium ; while thorium shows no signs of a valency less than four. The trivalency of cerium and praseodymium is of course due to a different cause, and does not concern us here.

GROUP V

Elements and atomic volumes :[1]

	V 23	Nb 41	Ta 73	Pa 91	A.
	9·3	13·3	16·8	—	
N 7	P 15	As 33	Sb 51	Bi 83	B.
(15·7	13·3	13·2	18·7	21·4	
at B. Pt.)	16·9	16·0	23·0		

A : (C)(11)2 or (C)(12)1. B : (C)(18)2,3.

The general relations are characteristic of all the later groups. The typical elements belong clearly to B and not to A ; A resembles B only in those compounds in which the atoms have the group valency. In their lower valencies the elements of subgroup A should not be compared with the other elements of this group, but with the A elements of groups IV and VI. It is therefore better to treat the two divisions of the group separately.

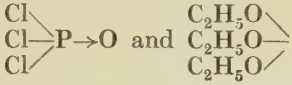
Typical Elements and Subgroup B

This is the first group in which we meet with mixed octets. The ordinary valency of the atoms is three (as in NH_3), the five valency electrons being increased to eight by the formation of three normal covalencies, giving the valency group 2, $\underline{3}$, $\underline{3}$. (The formation of simple cations with an electrovalency of five in anything but the minutest quantities is of course impossible.) The covalency can be increased to four, with the production of a fully shared octet, either by co-ordination as in $(CH_3)_3N{\rightarrow}O$, or by loss of an electron as in $[NH_4]^+$. By the expansion of the octet, except in nitrogen where this is forbidden by the covalency rule,[2] a covalency of five can be reached, as in PF_5, and this can be increased to higher values by co-ordination. A covalency of five (like all odd covalencies) is as a rule comparatively unstable, but it is more stable with elements of group V than elsewhere, since they can form it by the normal sharing of the five valency electrons (with five others from the attached groups) without the electrostatic disturbance caused by co-ordination. Even in this group, however, it readily goes over into the octet form wherever

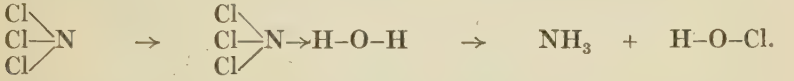
[1] Where two values are given for one element they refer to allotropic forms.

[2] For the evidence that nitrogen cannot have a covalency of more than four, see p. 153.

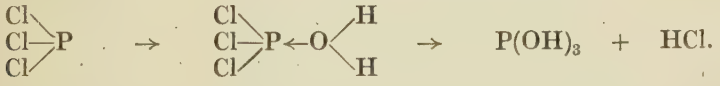
the nature of the attached atoms permits. It is almost confined to the pentahalides : in those oxygen compounds in which the atom is ordinarily written with a double link to oxygen, we have evidence (confirmed by the observation of the parachor[1]) that the link is really co-ordinate, and the atom 4-covalent, as in



The elements of this series are remarkable for occurring in two well-marked allotropic forms, a less dense transparent form, usually low-melting and more soluble in non-associated organic solvents, and a more dense, opaque, and more or less metallic form. The latter becomes increasingly stable as the atomic number rises ; it is non-existent in nitrogen, and is the only form in bismuth. The transparent form is always metastable except in nitrogen ; but it is least so in phosphorus and most in antimony. The metallic character and the tendency to ionization increase down the series, as is shown, for example, in the behaviour of the halides with water. That of nitrogen is peculiar ; as we have seen, the nitrogen, since it cannot increase its octet, must act as a donor in co-ordinating with the water, and so attach itself to the hydrogen of the latter. This causes hydrolysis to hypochlorous acid and ammonia :



With the other elements the octet can expand, and so the water can co-ordinate through the oxygen, which it is always more ready to do :



This leads to hydrolysis to hydrochloric acid and the hydroxide, unless the central atom can exist as an ion. With phosphorus the hydrolysis is complete, with arsenic less so ; with antimony the main product is the univalent ion $[Sb=O]^{+}$, with some Sb^{+++} ion ; with bismuth similar changes occur, but the Bi^{+++} ion is much more stable.

The affinity for hydrogen falls off in the normal manner, from the very stable ammonia to bismuth hydride, which decomposes

[1] See p. 127.

at the ordinary temperature with a half life period of some 20 minutes. The basicity of these hydrides falls off in the same way, phosphine being a very weak base, and the other hydrides scarcely basic at all. This is no doubt a direct result of the diminishing affinity for hydrogen, since the basicity depends on the formation of a fourth hydrogen link in $[XH_4]^+$.

The stability of the true 5-covalent compounds such as the pentahalides also diminishes with rise of atomic number, but apparently with some irregularity. Phosphorus forms pentahalides with fluorine, chlorine, and bromine (the stability diminishes as the atomic weight of the halogen increases) arsenic only with fluorine, antimony with fluorine and chlorine and in complexes with bromine, while bismuth forms none at all. But mixed alkyl or aryl halides such as $(CH_3)_3AsCl_2$ are formed by all four elements ; compounds of this type (with aryl, not with alkyl groups) afford the only known examples of 5-covalent bismuth, and these are very unstable.

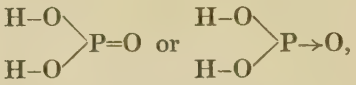
There is a certain ambiguity about the structure of the trivalent atoms of elements of this group. On the analogy of the neighbouring groups we should expect to find a tendency in the heavier elements for two of the valency electrons to become inert and behave as part of the core. This would reduce the valency to three, and make the atoms resemble those of the third group elements, in which there are only three valency electrons. On the other hand the same valency of three can arise through the formation of a mixed octet 2, 3, 3. In nitrogen and the earlier members generally there is no reason to suppose that the trivalency has any other cause than mixed octet formation. But with the later members, and especially bismuth, there is evidence that the inertness of the N_{11} pair is operative, and that the atoms are in a state resembling that of a third group element such as yttrium or lanthanum. This evidence is of various kinds ; there is the metallic nature of the element itself, and the existence of simple ions such as Bi^{+++}, which has the structure (60) (18) (2), which could hardly be stable unless the last two electrons were inert. So too the stable ' yl ' ions $[Sb{=}O]^+$ and $[Bi{=}O]^+$ have the E.A.N. (C)(18)(2,2,2), with a mixed sextet scarcely known elsewhere except in such atoms as that of divalent carbon, where it is explained by the strong tendency of the N_{11} grouplet to be inert in the elements of the fourth periodic group. There is further the tendency, which is increasingly strong in the heavier members of the subgroup, to form complexes derived

from the simple trivalent compounds, such as $K[BiCl_4]$, $[BiBr_3,2NH_3]$, and $K_3[Bi(CNS)_6]$. The effective valencies (see p. 164) of the bismuth atoms in these compounds are 5_4, 7_5, and 9_6 respectively, so that their valency groups are 10_4, 12_5, and 14_6, or (2,4,4,) (2,5,5), and (2,6,6). The occurrence of mixed valency groups of more than 8 electrons is practically if not absolutely confined to elements in which on other grounds we have reason to expect the N_{11} pair to be inert. That in this subgroup E.A.Ns of this form are abundant among the compounds of bismuth, not uncommon among those of antimony, but with one or two doubtful exceptions absent from those of the lighter elements, is a further confirmation of this view, since the inert pair is always more marked in the heavier elements of a group. There are other points of resemblance between bismuth and the metals of the third group, especially the formation of a series of complex nitrates of the formula $M''_3[M'''(NO_3)_6]_2$, $24H_2O$, in which M″ is magnesium, zinc, cobalt, or nickel. M‴ may be either bismuth or lanthanum, cerium, praseodymium, neodymium, samarium, or gadolinium.

Nearly all the elements of this series form a certain number of ' anomalous ' compounds, in which they show valencies which cannot be explained in the present state of our knowledge. Nitrogen gives the familiar nitric oxide NO and nitrogen dioxide NO_2, both of which are ' odd molecules ' and are paramagnetic. Analogous organic derivatives $(C_6H_5)_2N$ and $(C_6H_5)_2NO$ are known. Nitrogen dioxide from its tendency to polymerization may perhaps be compared with triphenyl methyl; both, if we write the nitrogen compound $N\begin{matrix}O\\ \searrow\\ O\end{matrix}$, have the same valency group, a septet (1, 3, 3) ; the di-aryl nitrogens Ar_2N, which also polymerize readily, may be referred to the same type. Nitric oxide, if it is correctly written N=O, also has a septet (3, 2, 2) ; but it shows a stability which it is difficult to reconcile with so unusual a structure. It is, of course, easy to write the molecule so that it has two complete octets, if we assume that the nitrogen shares three electrons belonging to the oxygen, and the oxygen two belonging to the nitrogen ; but this involves the assumption of a link of five shared electrons, which we have no other reason to suppose to be stable.

Phosphorus gives an anomalous compound in hypophosphoric acid H_2PO_3. It is easy to formulate this if we are allowed to double its formula, but the evidence, both from the conductivity

of solutions of the salts, and from the molecular weight in solution of its esters R_2PO_3, is in favour of the simple formula. If this is adopted, we cannot reconcile it with any recognized valency of phosphorus ; the acid may be written either



assigning to the phosphorus a valency group either of (1, 4, 4), or (1, 3, 3). In the same way certain complex salts of antimony have been described which are derived from a tetrahalide SbX_4, such as $Rb_2[SbCl_6]$ and $(NH_4)_2[SbBr_6]$.

At present we can do no more than note the existence of such anomalous compounds.

Subgroup V A : Vanadium, Niobium, Tantalum, Protoactinium

Melting-points of elements, and boiling-points of pentahalides :

	V	Nb	Ta	Pa
M. Pt. of Element	1730°	1950°	2800°	—
B. Pt. of XF_5	111°	220°	229°	—
B. Pt. of XCl_5	—	241°	242°	—

These elements show the characteristic valency relations of an A (transitional) subgroup. They have amongst them all possible valencies from 2 up to the group valency of 5, and it is only in this last state that they show any resemblance to the elements of the B subgroup. The metallic characteristics are confined to the lower states of valency, since the smaller charge renders ionization possible, and it is particularly to be noticed that in their trivalent compounds they have no resemblance to trivalent nitrogen or phosphorus. This may be taken as evidence that trivalent vanadium, for example, in its covalent compounds has not a mixed octet (2, 3, 3), as nitrogen and phosphorus have in NH_3 or PCl_3, but a sextet (3, 3), the other two potential valency electrons forming part of the core : (2) (8) (10) 3,3.

In their quinquevalent compounds there is a general similarity between these elements and those of subgroup B. It is curious that just as arsenic shows less tendency to form pentahalides than either phosphorus or antimony, so vanadium, in the same

long period as arsenic, refuses to form a pentachloride like niobium and tantalum, although a pentafluoride has recently been discovered. The analogy between the two subgroups is chiefly shown in the derivatives of the ions XO_4. Vanadic acid, apart from its oxidizing power, which depends on the transitional character of the element, resembles phosphoric in many of its properties, as we should expect, but differs conspicuously from it in two ways. The various forms of phosphoric acid and their ions (ortho, meta, pyro) are relatively stable, and only change slowly into one another in solution. But with vanadic acid the corresponding changes are very rapid : the solution of a vanadate contains all the forms of ion in equilibrium, and can be made to precipitate a salt of any one of them by a suitable modification of the conditions. A similar ease of transformation is found among the esters, which is an almost unparalleled phenomenon. Secondly, whereas the ultimate effect of hydrolysis or acidification on a meta- pyro- or orthophosphate is to give orthophosphoric acid H_3PO_4 or its ions—the simple form with one phosphorus atom in the molecule—the opposite effect is produced on a vanadate. The simple form of ion VO_4''' is only stable in presence of excess of hydroxyl ion, and is converted by hydrolysis or acidification through the increasingly complex forms of pyro- V_2O_7'''', meta- V_3O_9''' and hexavanadate V_6O_{17}'''', finally into the highly polymerized vanadium pentoxide $(V_2O_5)_n$, which is scarcely soluble in water, and forms no crystalline hydrates. This may be compared with the behaviour of a chromate, which gives on acidification the polymerized bichromate ion Cr_2O_7''.

In comparing the members of the subgroup with one another, we find, as in subgroup IV A, that there is a marked difference between the first member (first long period) and the second and third, which resemble one another closely, though not so closely as zirconium and hafnium. Of the last member, protoactinium, little is known beyond the fact that it resembles its predecessor tantalum. The relations are best illustrated by comparing the properties of niobium and tantalum with those of vanadium.

Niobium and tantalum always occur together in nature, and it was long before any satisfactory method of separation was discovered. The first point of difference from vanadium is in the stability of the lower valencies. Vanadium forms quite definite series of di-, tri-, and quadrivalent compounds. It was formerly thought that niobium could be quadri- and tri- but not divalent, and tantalum quadri- but neither tri- nor divalent. Recent work

has however shown that the relations are not quite so simple. Niobium can certainly be quadri- and trivalent. With tantalum the facts are less clear, but it is certainly sometimes trivalent, and probably quadrivalent ; and it is remarkable that there is definite evidence of divalent tantalum, though none of divalent niobium.[1] It still however remains true that in subgroup V A as in IV A the lower valencies are more stable in the first member than in the two following.

The quinquevalent oxy-acids (vanadates, niobates, and tantalates) have a common tendency to form condensed or polymerized ions, but vanadic acid is much stronger than the other two : the alkaline niobates and tantalates are decomposed by carbon dioxide with precipitation of the pentoxide. This is even more marked in the complex acids ; those of vanadium are much stronger than the original acid, while those of niobium and tantalum are not. In this respect the niobates and tantalates resemble the titanates, zirconates, and stannates more than the vanadates. This is an example of the increasing basicity of the heavier members which is common to all A and B subgroups ; in the same way the phosphates are more acidic than the arsenates, and these than the antimonates.

Another difference which may be referred to the same general tendency is the increasing affinity for halogens as compared with oxygen. Vanadium forms no pentachloride or pentabromide, but it forms both $VOCl_3$ and VO_2Cl : niobium forms $NbCl_5$ and $NbOCl_3$, but the evidence for NbO_2Cl is very weak : tantalum forms a pentachloride and a pentabromide, but no oxy-halides at all. If the pentoxides of the three elements are dissolved in hydrofluoric acid of the same concentration, and an alkaline fluoride MF is added, the salts which separate most easily are

with vanadium : VO_2F, xMF, $y H_2O$
with niobium : $NbOF_3$, xMF, $y H_2O$
with tantalum : TaF_5, xMF, $y H_2O$.

The fluoxytantalates, unlike their vanadium and niobium analogues, can only be prepared in the absence of free hydrofluoric acid, which converts them into the fluotantalates.

[1] The spectroscopic evidence (p. 46) shows that the penultimate electronic group is more stable in the second transitional series of elements (Zr–Pd) than in the first (Ti–Ni) or the third (Hf–Pt), and that while vanadium and tantalum have in the ' normal ' state two electrons in the outermost quantum group, niobium only has one.

GROUP VI

Elements and atomic volumes :

	Cr 24	Mo 42	W 74	U 92	A
	7·5	11·2	9·6	12·8	

O 8	S 16	Se 34	Te 52	Po 84	B
14·3	15·6	16·5	20·6	—	
(at B. Pt.)	16·4	17·6			

A : (C)(12)2 or (C)(13)1. B : (C)(18)2,4.

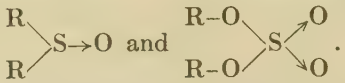
The elements of the A subgroup again have smaller atomic volumes than those of the B, and the difference is more marked than in group V ; it is no doubt due to the metallic structure and closer packing of the A elements. The resemblance of the A elements to the others becomes more restricted in each successive group, as the highest valencies become less important.

Typical and B Elements

This is the first group in which we find monatomic anions. On the Fajans theory, ionization in this sense should take place more easily in the later members of the group, but the difference in size is not great. On the other hand the later elements, especially tellurium, can form quadrivalent cations : this is due to the inertness of the N_{11} pair, which reduces the available valency electrons to four, and makes the element behave like a fourth group metal such as tin, the Te^{++++} ion, with a structure (2) (8) (18) (18) (2), having a stability approaching that of the stannic ion (2) (8) (18) (18).

The covalent compounds are of more interest. The elements have a covalency of 2 in mixed octet formation (4, $\underline{2}$, $\underline{2}$), as in H_2S, and by loss of an electron can form a tricovalent complex cation, as in the oxonium and sulphonium salts, such as $[(CH_3)_2O{\cdot}H]X$ and $[(CH_3)_3S]X$. There is less tendency to form oxonium or sulphonium than ammonium salts, presumably because the former lack the stability of the 4-covalent atom. A covalency of 3 and even of 4 may be attained by co-ordination : oxygen, whether as hydroxyl or in the groups C—O—C or C=O, is very ready to form such a link. A second co-ordinate link (making a covalency of 4) is rare with oxygen, but occurs in such compounds as the basic beryllium acetate ; it is commoner with the heavier elements. With the exception of oxygen all

these elements can form a valency group of 12 (tellurium of 16), as in the hexafluorides, but most of them assume the octet form where possible, as in the sulphones and sulphuric esters



This tendency to prefer the octet is however less marked than in group V, presumably because a covalency of 5 (decet), which with the latter element is the alternative to the octet, is less stable than a covalency of 6. There is evidence from the parachor (p. 129) that sulphur trioxide is at least partially in the 6-covalent form, and in telluric acid (see below) this is the stable form, and not the 4-covalent as in selenic and sulphuric acids.

The main differences between oxygen and sulphur are as follows:

(1) Sulphur is more acidic than oxygen, as may be seen by comparing water (dissociation constant 2×10^{-16}) with hydrogen sulphide (first dissociation constant 10^{-7}, second 10^{-15}), or alcohols with mercaptans, or amides with thioamides. This is the opposite of what we should have expected on general grounds and on the Fajans theory: it may perhaps be due to the much smaller association of –S–H as compared with –O–H, discussed below under (4).

(2) The link between sulphur and sulphur is much stronger than that between oxygen and oxygen, and in consequence sulphur is much more ready to form long chains. The existence of S_8 molecules in the vapour and in solution, while oxygen is O_2 or in the metastable form O_3, is evidence of this. In compounds no examples of a chain of more than two oxygen atoms are known except the very unstable ozonides, and even compounds with two linked oxygen atoms, such as hydrogen peroxide and the organic peroxides and per-acids, decompose very readily. Chains of two, three, and even more sulphur atoms (as in the polysulphides) are readily formed and are stable. These relations are the reverse of those observed in group IV, where the first element carbon forms far more stable and longer chains than the second silicon.

(3) Sulphur has a much stronger tendency to assume a valency greater than two. It can of course exert a covalency of six, while oxygen is limited to four; but even in the compounds in which sulphur retains its octet, it shows a much

greater stability with covalencies of three and four than does oxygen. The comparison of the sulphonium and oxonium compounds illustrates this, and we have also such compounds as the sulphoxides, sulphones, and sulphates, to which oxygen offers no analogy.

(4) A curious difference is that while the hydrogen of a hydroxyl group readily acts as an acceptor, that of a sulphydryl group –S–H has no such power. Hence hydrogen sulphide and the mercaptans are not associated, as may be seen by comparing their boiling-points with those of their oxygen analogues (those of ethyl ether and diethyl sulphide are added to show the normal effect of the greater atomic weight of sulphur) :

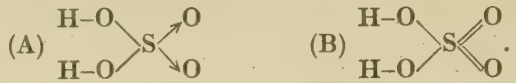
	Boiling-points			Difference
H–O–H	100°	H–S–H	–60°	+160°
CH_3–O–H	66°	CH_3–S–H	+6°	+60°
C_2H_5–O–H	78°	C_2H_5–S–H	+36°	+42°
(C_2H_5–O–C_2H_5	35°	C_2H_5–S–C_2H_5	92°	–57°)

In the series sulphur—selenium—tellurium we find the usual fall in the affinity for hydrogen and increase in the metallic character as the atomic number rises. This last change is largely due to the increasing stability of the form in which the first two valency electrons behave as part of the core. This may be seen by considering the quadrivalent compounds. Some of these are really octet compounds with a co-ordinate link, like the sulphoxides $\begin{matrix}R\\R\end{matrix}\!\!>\!S\rightarrow O$, and need not be further discussed ; but in such substances as the tetrahalides the valency group has increased by four, and so must have the form (2, 4, 4). Again in the quadrivalent ions such as Te^{++++} the core contains two electrons more than the complete groups (48 electrons instead of 46). Such structures are scarcely possible unless these two unshared electrons are, in the sense in which we have used the word, inert. We should therefore expect them to be more prevalent in the heavier elements, and this is found to be so. The only definite sulphur compound of this type[1] is the tetrachloride, which decomposes at –40° ; selenium forms a tetrafluoride (B. Pt. + 100°), and a tetrachloride which is stable up to high temperatures. The tellurium compounds are still more stable ; they include such substances as the tetrachloride (M. Pt. 224°, B. Pt. 414°), the tetrabromide (M. Pt. 380°, B. Pt. ca. 420°), and the

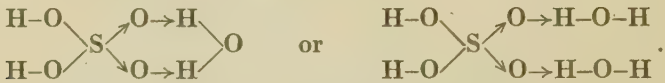
[1] We may assume that sulphur dioxide has the structure O=S→O.

dimethyl diiodide $(CH_3)_2TeI_2$, remarkable for existing in two isomeric forms, showing that the four attached groups lie in a plane (p. 231). The tetrachloride behaves in the fused state as if it were at least partially ionized ; at its melting-point it has the conductivity of a salt (0·115 at 236°). Still more like salts are the quadrivalent compounds of the oxy-acids, such as $Te(NO_3)_4$ and $Te(SO_4)_2$, which show the existence of the quadrivalent cation Te^{++++}.

There is a remarkable difference between telluric acid and its selenium and sulphur analogues. Sulphuric acid might have either of two formulae



It combines with water with great readiness : if it had the first formula we should expect its hydrates to be formed by coordination, and to have such formulae as



If it had the second structure (B), the hydration should involve the conversion of the doubly linked oxygen into two hydroxyl groups, giving $O{=}S(OH)_4$ and $S(OH)_6$. In the latter case the compound should be able to act as a tetra- or hexabasic acid, but of this there is no indication.[1] We may therefore assume that sulphuric acid has the first structure (A), and that its hydrates are formed by co-ordination. This conclusion has recently been confirmed by the measurement of the parachors of the alkyl sulphates. Selenic acid behaves like sulphuric, and must have the corresponding structure. Telluric acid, on the other hand, is quite different. H_2TeO_4 does not exist at all. The acid is precipitated from the aqueous solution of one of its salts in the form usually written H_2TeO_4, $2H_2O$, that is as $Te(OH)_6$. This does not lose water below 140°, and when it does, it goes straight to the trioxide without any intermediate formation of H_2TeO_4. The formula $Te(OH)_6$ is further supported by the formation, on methylation with diazomethane, of an ester $Te(O{\cdot}CH_3)_6$. The ordinary tellurates all contain at least two molecules of water, which cannot be removed without deep-seated decomposition : these are ob-

[1] Unless the existence of compounds such as turpeth mineral $HgSO_4{,}2HgO = Hg_3SO_6$ is to be taken as proof that this structure can occasionally be assumed.

viously of the form $K_2H_4TeO_6$. There are also tetrabasic salts such as $Na_4TeO_5,8H_2O$, which should be written $Na_4H_2TeO_6$, $7H_2O$, and hexabasic, as Ag_6TeO_6 and Zn_3TeO_6. It is to be noticed that the next element to tellurium behaves in the same way: periodic acid is not HIO_4 but H_5IO_6. This change in behaviour is not likely to be due to the double link to the oxygen being more strained when it is attached to one of the heavier elements: it is more probable that the octet form becomes less stable as the covalency maximum increases.

Subgroup VI A: Chromium, Molybdenum, Tungsten, Uranium

Boiling-points of polyhalides:

X =	Cr	Mo	W	U
XCl_5	—	268°	276°	—
XBr_5	—	—	333°	—
XF_6	—	35°	19·5°	56°
XCl_6	—	—	347°	—

In compounds in which they have the group valency of six these elements show the usual resemblance to those of the B subgroup. All except chromium form very volatile hexafluorides, and all form stable acids of, or derived from, the type H_2XO_4. These acids show a steady fall in acidity with increasing atomic number, as we should expect: they also, like those of the elements of subgroup V A, have a tendency to condense, which is noticeable even in the first of them (in the formation of bichromic acid), and is especially marked in molybdic and tungstic acids, where it leads to the formation of the enormous and complicated group of the heteropoly-acids and their salts, of which $K_4H_4[Si(W_2O_7)_6],16H_2O$ is an example. In their general properties there is a close resemblance between molybdenum and tungsten (as there is between niobium and tantalum, and still more between zirconium and hafnium), while these elements differ much more from chromium on the one hand and uranium on the other.

The formation of polyhalides in this series is peculiar. All the members except chromium form very volatile hexafluorides, tungsten a hexachloride (the only known compound XCl_6), and molybdenum and tungsten also give pentahalides. Chromium forms neither penta- nor hexahalides; in this it resembles vanadium and arsenic (which give no pentahalides except with

fluorine), so that the instability of this form of molecule seems to be common to the elements of the first long period.

The elements have every possible valency from two to six; as the atomic number increases, the stability of the lower valencies diminishes, and where they occur, the compounds tend to be covalent and not ionized. Apart from the group valency of six, which they all exhibit, the most important valencies are: for chromium two in the unstable chromous and three in the stable chromic ion: for molybdenum a valency of two is confined to derivatives of Mo_3Cl_6, whose structure is still obscure, although it behaves in some ways as a salt $[Mo_3Cl_4]Cl_2$: valencies of three and five are definitely established, and four is probable: with tungsten two, three, and four are probable but certainly unstable, while five is well established; with uranium, valencies of two and three are excessively unstable, while that of four occurs in a form unknown in the lighter elements, that of a simple ion U^{++++}, which undoubtedly exists, although it is readily oxidized to the much more stable uranyl ion. A valency of five with uranium is uncertain, depending on such compounds as the pentachloride, which is solid, and may be a compound of the tetrachloride and hexachloride. Uranium is peculiar in forming the very stable uranyl ion $[O=U=O]^{++}$; this may be compared with such ions as zirconyl $[Zr=O]^{++}$, and it is to be noticed that just as ions of the zirconyl type, with one doubly linked oxygen, are not formed by the lighter elements, so the uranyl type, with two such oxygen atoms, only occurs with the heaviest.

GROUP VII

Elements and atomic volumes:

	Mn 25	Ma 43	Re 75		A.
	7·4	—	—		
F 9	Cl 17	Br 35	I 53	(85)	B.
16·7	22·2	25·1	25·6	—	
(B. Pt.)	(B. Pt.)	(0°C.)			

A: (C)(13)2 or (C)(14)1. B: (C)(18)2, 5.

The resemblance between the subgroups, being limited to compounds in which the elements have a valency of seven, is only found in the ions $[XO_4]^-$ and their derivatives.

Typical Elements and Subgroup B : Halogens

The halogens, having one electron less than an inert gas, form as well marked a series as the alkali metals, which have one electron more ; but their behaviour is more diverse, because it is not confined, as that of the alkali metals practically is, to the properties of the simple ions, but includes the formation of covalencies, which varies along the series, being largely affected by the atomic number. The one electron needed to make up the inert gas number is readily acquired either by transference or by sharing : the halogens form stable univalent compounds, both ionized and covalent, the former distinguished from the latter by their low volatility and high conductivity in the fused state and in ionizing solvents. The relative stability of these two forms depends both on the positive and on the negative constituent. The influence of the former is indicated by Biltz's measurements of the electrical conductivity of the fused chlorides (p. 105). Briefly, he found that nearly all the chlorides had a conductivity at the melting-point either greater than 0·1 (ohm^{-1} $cm.^{-1}$) or less than 10^{-6}. Among the typical and A elements good conductors are formed by all those of the first group except hydrogen, all of the second except beryllium, all of the third except boron and aluminium, and none of the fourth except thorium. Most of the other elements when exerting their group valencies form practically non-conducting halides. The B elements follow the same general lines, but the conductivities are smaller. The only chlorides with conductivities between 0·1 and 10^{-6} are beryllium chloride (0·0032), zinc chloride (0·01) and mercuric chloride (0·0008). The nature of the linkage is largely dependent on the conditions, and many of the chlorides which are bad conductors in the fused state are highly ionized in water, such as hydrochloric acid, aluminium chloride, and stannic chloride. The general conclusions are those required by Fajans' theory, ionization being promoted by small charge and large size of the cation.

The influence of the size of the halogen is in the opposite direction ; the larger it is, the more readily it should form covalencies. The atomic volume, being derived from the covalent free halogen, throws little light on the size of the ion. But the X-ray measurements of the fully ionized crystals of the alkaline halides show clearly that the diameter of the chlorine ion is about 1 Å.U. greater than that of the fluorine ion, and that a

further increase of about 0·4 Å.U. occurs when we go from chlorine to bromine and from bromine to iodine. We should thus expect that fluorine would ionize most readily, and that iodine would have the strongest tendency to form covalent compounds. This is in complete agreement with observation. There are many metals, such as aluminium, tin, and mercury, of which the fluorides have the high boiling-points of salts, while the other halides behave as covalent compounds, and a further example is found in the halides of silver, of which the chloride and bromide have in the crystal an ionic lattice, while the iodide (in one form at least) has a molecular lattice. The same thing is seen in the formation of higher covalencies : those of five and six are limited to iodine, and a covalency of three, apart from the oxy-acids, is rare with bromine, almost unknown with chlorine, and quite unknown with fluorine.

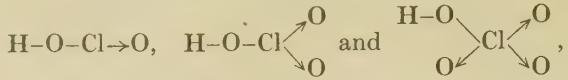
As is usual, the affinity for hydrogen falls off greatly as the atomic number increases, as is shown by the familiar change in the heat of formation of the gaseous hydrides (HF + 38·5, HCl + 22·0, HBr + 8·6, HI − 6·4 kgr. cals.). The great affinity of fluorine for hydrogen explains some of its more puzzling peculiarities. The affinity for oxygen increases on the whole, but irregularly : fluorine forms no compounds in which it is attached to oxygen (no oxides and no oxy-acids) ; chlorine forms oxides (unstable, and including the anomalous dioxide ClO_2 with its odd molecule), and oxy-acids up to the very stable perchloric acid; bromine forms no oxide and no perbromic acid, and even in the HXO_3 stage seems to have less affinity for oxygen than either chlorine or iodine (heats of formation of HXO_3 aq. : $HClO_3$ 23·0, $HBrO_3$ 12·5, HIO_3 56·0 kgr. cals.). Iodine forms a stable pentoxide, and very stable oxy-acids up to H_5IO_6, in which the iodine is attached to six oxygen atoms. The refusal of bromine to form to 4-covalent HXO_4, while chlorine and iodine do so, may be compared with the instability of other members of the same period, such as vanadium, chromium, and arsenic, in the 5-covalent state.

In their covalent compounds the halogens show in general a progressive change of properties. As with the alkali metals, the highest observed covalencies are definitely below the theoretical maxima ; this is shown by the following list, in which the maxima according to the covalency rule are added in brackets : fluorine 2 (4), chlorine 4 (6), bromine 3 (6), iodine 6 (8). In their general behaviour, chlorine and bromine are similar, and differ

in many ways from fluorine on the one hand and iodine on the other. Fluorine has four marked characteristics : (1) its great tendency to ionization, already mentioned ; (2) its great affinity for hydrogen ; (3) its very low covalencies ; (4) its tendency to combine with other atoms up to their highest covalency values. These sometimes conflict with one another. The only compound in which it certainly has a covalency greater than one is the polymerized hydrofluoric acid. This acid at its boiling-point (19·4°) has a vapour density approaching that of H_4F_4, although at 90° it is practically entirely HF, and there is no evidence of the existence in water of any molecule containing more than two fluorine atoms. The highest polymer must contain the grouping F–H←F–H←, with 2-covalent fluorine, but this is evidently unstable. In water hydrofluoric acid occurs as the single and double molecules HF and H_2F_2, or their ions. It has been shown that while the polymerized form is a strong acid $H[F_2H]$ and is wholly ionized, the true dissociation constant of the simple HF is only 7×10^{-4} (about three times that of formic acid, and about half that of monochloracetic), so that the weakness of hydrofluoric acid as compared with the other halogen acids is only partly explained by its polymerization. This conclusion, that whereas the other halogen hydrides are practically completely ionized in water, hydrogen fluoride is mainly covalent, is particularly surprising in view of the greater tendency in general of fluorine to ionization, which is established both practically and theoretically. It would seem that this is overcome in the case of the hydrogen compound by the unusual strength of its covalent link to hydrogen. The same thing seems to account for the peculiar tendency of the fluorine ion to hydrate, as is shown by the existence of hydrated fluorides of potassium and silver, two metals of which the salts are normally anhydrous : the fluorine ion, being negative, will of course attach itself to the hydrogen of the water. The last peculiarity of fluorine is that while its own covalency is unusually low, it tends to bring out the highest covalencies of the other atoms with which it combines. This is illustrated by such compounds as $[F_2H]^-$, AsF_5, IF_5, SF_6, SeF_6, and OsF_8, to which the other halogens offer no analogues. The cause of this may very well be the small size of the fluorine atom ; but whatever the cause, the fact is very marked.

The other halogens readily assume a covalency of more than one, and do so on the whole with greater case as the atomic

number increases. Many such compounds are derived from the simple octet by co-ordination, as in



of which the last is the most stable. These types are also formed by iodine, and all except the last by bromine. The normal form of periodic acid (and the periodates) is different, but the 4-covalent structure must be assumed, for example, in the crystalline HIO_4, and in anhydrous $K[IO_4]$. Iodine can also assume a covalency of two in a different way (still retaining the octet), by losing an electron and forming an iodonium ion, as in the aromatic derivatives $[Ar_2I]X$: the corresponding hydroxide is a strong base. These compounds are structurally analogous to the ammonium and sulphonium bases; they are not very stable, and are almost if not quite limited to the aromatic compounds. No other halogen can behave in this way. Periodic acid shows a tendency, precisely like telluric acid, for the iodine to pass into the 6-covalent form, with the expansion of the octet to a duodecet: it crystallizes from water as H_5IO_6 (although this can be dehydrated to HIO_4) and gives a series of salts $M'_5IO_6 = (MO)_5I{\rightarrow}O$, and another series $M'_3\,IO_5 = (MO)_3I\langle^{O}_{O}$ (these are written for convenience in the non-ionized form), as well as more complicated condensed types, such as $M'_4I_2O_9$. In these compounds the iodine has the normal core, its E.A.N. being (2) (8) (18) (18) **6**, **6**: that of tellurium in the tellurates (p. 286) is the same.

So far, the structures of the halogen atoms in their compounds are of the normal type. There are, however, other compounds in which the structure cannot be explained except on the assumption that two of the original seven valency electrons are inert, and behave as part of the core, which takes the form (C) (18) (2). This behaviour is to be expected, from the analogy of other groups, among the heavier members of the series, and in fact such compounds are almost confined to iodine. The absorption of two of the valency electrons into the core would make the element behave like one of the fifth group such as antimony, just as it makes tellurium behave somewhat like tin. The most familiar examples of such compounds are the polyhalides, such as $K[I_3]$ and $Cs\,[ICl_2]$. The ion of the latter evidently has the structure $I\langle^{Cl}_{Cl}$, and this is confirmed by X-ray observations; two

of the halogen atoms are in the normal 1-covalent form, and the third, which is in an abnormal state, links them together. This third atom having gained three electrons, one from the charge and one from each of the other two halogen atoms, has ten electrons outside the normal core of 46, four of them being shared. The resulting form (6, 2, 2)—a mixed decet—is, as we have seen, almost unknown except when two of the unshared electrons can be regarded as part of the core. Since the inertness of the first pair increases with the atomic weight, the heaviest halogen in a mixed perhalide will always form the link. Any halogen except fluorine can form part of a perhalide; the stability is greatest if one of the atoms is iodine, much less if the heaviest is bromine, and very small in the trichlorides. More complicated perhalides (up to $[hal_9]^-$) are known, but few of them have been shown to exist in any but the solid state. A similar structure must be assumed for such compounds of trivalent iodine as the trichloride ICl_3, the aryl iodide-chlorides $Ar{-}I\langle^{Cl}_{Cl}$, the iodoso-compounds Ar–I=O, and their acetates

$$Ar{-}I\langle^{O\cdot CO\cdot CH_3}_{O\cdot CO\cdot CH_3}.$$

On the assumption of a core of 46 + 2, all these have mixed octets (2, 3, 3). The analogy to the fifth group elements is further shown in the 5-covalent pentafluoride IF_5 (boiling-point 97°, vapour stable up to 400°), in which the iodine has the E.A.N. (46 + 2) 5, 5. The iodoxy-compounds $ArIO_2$ can either be written as 4-covalent $Ar{-}I\langle^{O}_{O}$, on the analogy of the nitro-compounds, or as 5-covalent $Ar{-}I\langle\!\langle^{O}_{O}$. In either case they have the increased core of 48.

An unexplained anomaly is the formation of double salts from iodine trichloride. If the iodine in this has the structure (48) (2, 3, 3), it should be capable of acting as a donor but not as an acceptor. It forms, however, a series of salts of the type $K[ICl_4]$, and the stability of the trichloride in strong hydrochloric acid suggests the formation of an acid $H[ICl_4]$. In this ion the central atom has 12 electrons in addition to a core of 46, of which 8 are shared. Even if we assume that two of them are inert we are left with the mixed decet (2, 4, 4), to which there is scarcely any parallel.

Subgroup VII A : Manganese, Masurium, Rhenium.

The last two elements have recently been discovered by means of their characteristic X-rays in platinum ores, in columbite, and probably also in manganese ores ; but scarcely anything is known of them except that they are less easily precipitated by hydrogen sulphide than manganese, and that they form volatile oxides. Our knowledge of the subgroup thus rests on the behaviour of manganese.

Manganese exhibits valencies of 2, 3, 4, 6, and 7 : that is, the third quantum group in the core can contain 13, 12, 11, 9, and 8 electrons : the core (2) (8) (10), which does not occur with manganese, is very unstable with chromium (Cr^{iv}). In the two highest valencies it is definitely acidic, in the two lowest (and to a considerable extent in its quadrivalent compounds) it is metallic. It resembles the halogens in its highest state of oxidation only, the permanganates being isomorphous with the perchlorates, and having nearly the same molecular volumes. Their chemical properties are, of course, very different, as the permanganates are readily reduced owing to the ease with which the valency electrons are absorbed into the core, which cannot happen with chlorine. A valency of six occurs in the manganates, as $Na_2\left[\begin{matrix}O\\O\end{matrix}\!\!>\!\!Mn\!<\!\!\begin{matrix}O\\O\end{matrix}\right]$, the hydrates of which are isomorphous with those of sodium chromate, and one of them with the corresponding sulphate. This valency is less stable, as the ion readily passes into that of the permanganate and manganese dioxide. The compounds of quadrivalent manganese are only known either in insoluble forms such as manganese dioxide, or in complexes such as $K_2[MnCl_6]$, which readily pass into forms of lower valency with loss of chlorine : no quadrivalent ion is known. The definite formation of cations is first observed in the next lower valency, that of trivalent manganese. This is also unstable, and the salts tend to hydrolyze to insoluble oxides or hydrates unless they are protected by complex formation. The salts of divalent manganese are stable, and are much less hydrolyzed ; in acid or neutral solution they are not affected by air, but in presence of alkali air rapidly converts them into more highly oxidized products. The behaviour of manganous and manganic salts is very similar to that of ferrous and ferric. The general tendency in the series of elements from titanium to nickel is for the stability of the divalent form as compared with the trivalent to increase with

rise of atomic number, but in respect to this property manganese does not quite come in its place. The divalent form is on the whole rather more stable in manganese than in iron.

GROUP VIII

Elements and atomic volumes :

VIII 1.	VIII 2.	VIII 3.
Fe 26	Co 27	Ni 28
7·1	6·8	7·1
Ru 44	Rh 45	Pd 46
8·4	8·5	9·3
Os 76	Ir 77	Pt 78
8·5	8·6	9·1

The three transitional triads, conventionally regarded as a single group, should properly be divided vertically into three series, distinguished, according to the number of electrons they have in excess of those in the preceding inert gas, as groups VIII, IX, and X. As, however, the convention is so firmly established these three divisions may be called subgroups VIII 1, VIII 2, and VIII 3.

The common view that the elements of a triad resemble one another far more closely than they do their immediate predecessors and successors is the result partly of this traditional grouping (which was itself largely due to a desire to secure greater apparent symmetry in the periodic table) and partly of the fact that there are no typical or B elements with which to compare them. Actually there are considerable differences between the successive members of each triad : the three vertical series have sufficient individuality to have enabled chemists to assign the correct chemical order to cobalt and nickel before their atomic numbers were known ; and at the same time these elements have many analogies both with the preceding elements and also with copper and gold in their higher valencies.

As will be seen from the table on p. 48 there is a difference between the three horizontal rows in the structure of the normal atom :

Fe (C) (14) 2	Co (C) (15) 2	Ni (C) (16) 2
Ru (C) (15) 1	Rh (C) (16) 1	Pd (C) (18) –
Os (C) (14) 2	Ir (C) (15) 2	Pt (C) (16) 2

In the first and third rows the outermost quantum group always contains two electrons, while in ruthenium and rhodium one, and in palladium both, of the last two electrons are in the previous electronic group. This difference in the stability of the penultimate group has a marked effect on the elements next after the triads, in the refusal of silver to follow copper and gold in reaching a valency greater than one ; but it is less easy to trace its chemical influence on the elements of the triads themselves, probably because their valency relations are altogether more complicated. It is obvious that in solid elementary palladium the structure cannot be the same as in the isolated atom ; the metal is a conductor, and must be formed of positive ions (in which the 18 group has broken down) and electrons.

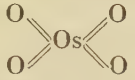
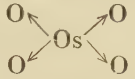
Certain progressive tendencies may be observed both in the horizontal and in the vertical series. In every vertical series we find, as in the A elements of the preceding groups, that with an increase of atomic number the lower valencies become less and and the higher more stable. This makes the elements become less metallic in their compounds as a whole, since the electropositive behaviour is connected with the lower valencies. Further, even when they have the same valency the successive elements of any vertical series show an increasing tendency to complex formation, as may be seen by comparing the compounds of divalent nickel, palladium, and platinum.

In the relations of the three vertical series to one another the most remarkable differences are in the increasing stability of the divalent as compared with the trivalent form, and the disappearance (except to a very limited extent with the heaviest member of each series) of all valencies greater than four, after we leave the first series.

It may be pointed out that none of these elements appears to be capable of a valency of five.

Subgroup VIII 1 : Iron, Ruthenium, Osmium

This subgroup is distinguished by the frequent occurrence of valencies of six and eight, especially in the heavier members. As these elements have eight electrons more than an inert gas they might be expected to show a valency of eight, especially in 8-covalent compounds, which could be formed directly without co-ordination. By the covalency rule this value is possible for ruthenium and osmium, but not for iron. Accordingly, we find

that osmium (alone among elements) forms an octofluoride OsF_8 (B.Pt. 47·5°). It is at least probable that we should assign a similar 8-covalent structure to osmium in the tetroxide OsO_4, and write it  and not  , or in any intermediate form. This is supported by the fact that ruthenium, which also can be 8-covalent, likewise forms a volatile tetroxide (B.Pt. 101° at 183 mm.), while iron, which is limited to a covalency of six, does not. The argument from the parachor against the 8-covalency of osmium in the tetroxide is, as we have seen (p. 128), inconclusive.

The chief change as we descend the series is the diminishing stability of the lower valencies and of the simple ions. The most stable valencies of iron are two and three (ferrous and ferric), practically the only other being six in the ferrates $K_2[FeO_4]$. The chief valencies of ruthenium are three and four, and the next most stable six and eight, while two and seven (but not five) rarely occur. In osmium the most stable are six and four, and then eight : three occurs rarely, but no others.

Subgroup VIII 2 : Cobalt, Rhodium, Iridium.

This subgroup is remarkable for the stability of the trivalent state (especially in complexes), and for the absence of the higher valencies, nothing being known above three for cobalt, four for rhodium, and six for iridium.

The behaviour of cobalt illustrates the effect which complex formation may have on the stability of a particular state of valency. The only form of simple (or hydrated) ion which is stable is the cobaltous : the only simple cobaltic salt known, the sulphate $Co_2(SO_4)_3$, rapidly changes in solution into the cobaltous salt, with evolution of oxygen; but in the 6-covalent form (as in the ammines) the cobaltic ion is extremely stable.

Rhodium occurs mainly in the trivalent form, which resembles the cobaltic ion in giving an enormous number of 6-covalent co-ordination complexes, but differs from it in being stable also as the simple ion. It is doubtful whether rhodium is ever divalent, but it can occur (which cobalt cannot) with a valency of four.

Iridium again is most stable in the trivalent state, practically always forming complexes. Higher valencies of four and six are

known, and compounds of divalent and even univalent iridium have been described, but their existence is doubtful.

Subgroup VIII 3 : Nickel, Palladium, Platinum.

All the members of this subgroup are stable in the divalent state.

The comparison of cobalt and nickel illustrates the increase of stability of the divalent state of these elements with rise of atomic number. It is doubtful whether trivalent nickel exists at all. In nearly all its compounds nickel is divalent, but a red complex cyanide of univalent nickel $K_2[Ni(CN)_3]$ has been prepared. Palladium again is nearly always divalent (and usually complex), but compounds are known in which it is tri- and quadrivalent.

Platinum is comparatively stable in the divalent state, but more so in the quadrivalent ; this is the normal increase of stability of the higher valencies with increase of atomic number in any subgroup. The complex derivatives of di- and quadrivalent platinum have been investigated in very great detail, and they illustrate the influence of the covalency on the stability of the valency. Nearly all the complexes formed by divalent platinum are 4-covalent (the four groups, as we have seen, lying in a plane), while those of quadrivalent platinum have a covalency of six.

There are also a few compounds in which platinum has a valency of six, and some in which it appears to have a valency of three.

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